

Polymer

ENGINEERING AND SCIENCE

POLYMER TOPICS

**RETEC: High Performance Engineering Materials
SPE Engineering Properties &
Structure Division & Ontario Section
October 16-17, 1985**

CONTENTS

- 445 Introduction
- 446 R.T. WOODHAMS/History and Development of Engineering Resins
- 453 D.D. CALLANDER/Thermoplastic Polyester Resins for Containers
- 458 D.C. CLAGETT and S.J. SHAFER/Polycarbonate Resins
- 462 R.W. AVAKIAN and R.B. ALLEN/Properties of a Transparent Polycarbonate Copolyester Blend
- 467 D.J. CORNELIUS and C.M. MONROE/The Unique Properties of Silicone and Fluorsilicone Elastomers
- 474 O.B. SEARLE and R.H. PFEIFFER/Victrex Poly(ethersulfone) (PES) and Victrex Poly(etheretherketone) (PEEK)
- 477 R.I. WARREN/Polyphenylene Ethers and Their Alloys
- 483 P.M. SUBRAMANIAN/Permeability Barriers by Controlled Morphology of Polymer Blends
- 488 D. KLEMPNER, K.C. FRISCH, X.Y. XIAO, and H.L. FRISCH/Two and Three Component Interpenetrating Polymer Networks

Continued on Back Cover



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ENGINEERING AND SCIENCE

Published by the Society of Plastics Engineers

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Polymer Engineering and Science (ISSN 0032-3888) is printed at Waverly Press, Easton, MD 21601. Address changes, undeliverable copies and orders for subscriptions should be sent to Circulation Manager, Society of Plastics Engineers, 14 Fairfield Dr., Brookfield Center, Conn. 06805. Published monthly except for February, April, June, August, October, and December when published semi-monthly. Second-class postage paid at Brookfield Center, Conn., and additional

entry offices. Accepted at special postal rate provided in P.M. Sec. 132.122.

Neither the Society of Plastics Engineers, Inc., nor **Polymer Engineering and Science** is responsible for the views expressed by individual contributors either in articles published in **Polymer Engineering and Science** or in technical papers presented at meetings of the Society.

Subscription rates for 1985. SPE members, 1 year—\$75, 2 years—\$135, 3 years—\$180. Nonmembers (U.S. and North America), 1 year—\$105, 2 years—\$180, 3 years—\$250. Corporate, Institutional or library, 1 year—\$275. Postage charge for all subscriptions outside North America—\$18 per year. Air delivery outside North America—\$50 per year.



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Business and Executive Offices, 14 Fairfield Dr., Brookfield Center, Conn. 06805

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POLYMER ENGINEERING & SCIENCE is indexed by:—Chemical Abstracts—Engineering Index, Inc.

INTRODUCTION

The 1984 RETEC on High Performance Engineering Materials was organized jointly by the SPE Engineering Properties and Structure Division and the SPE Ontario Section, the first partner being responsible for the technical program and the second for the local arrangements. The meeting was held on October 16 and 17, 1984, in Mississauga, Ontario. The 13 selected papers published in this issue provide an abbreviated version of what was presented at the RETEC.

It is customary to divide the commercial resins into three categories: commodity, engineering, and specialty plastics. However, these terms refer primarily to the volume of consumption (or price), not to any distinguishable set of physical parameters. Furthermore, there is no place in this classification for modified plastics of enhanced properties. This was the reason for selecting the theme and the title for the RETEC to be High Performance Engineering Materials (HiPEM's). Under this label one may list any material developed with a conscious effort of scientists and engineers to achieve some specific enhanced characteristics of the final product. The property may be tensile strength, shear modulus at elevated temperature (i.e. at 250°C), controlled permeability, chemo-mechanical effects, electrical conductivity, bio-compatibility, lubricity, pyrochromaticity, and so on. Some of these materials derive the properties from sophisticated polymer chemistry, some from compounding, others from special methods of processing or forming. It is important to recognize that frequently the enhanced properties (viz. electrical conductivity) can be obtained using different routes. This is why, in order to discuss HiPEM's, we had to bring together people with very diverse backgrounds.

With the annual growth rate in two digit figures, it is no doubt that HiPEM's constitute the fastest

growing segment of this economy. In absolute terms, by the end of this decade the value of high performance polymer alloys, blends, and composites alone will reach about one third of the value of all manufactured plastics. It is obvious that HiPEM's are of growing interest and importance to the plastics industry as well as to design engineers and materials scientists. These are truly the materials of the future. Judging by numerous discussions and phone calls there is a need for regular meetings on the subject.

The fact that engineering resins are designed for a particular application obviously restricts their usage. To extend the range of performance the resins are extensively modified by alloying and blending with other polymers as well as reinforcing with various fillers. During the last decade the application of traditional methods of metal shaping operations to plastics has gained popularity. Solid state extrusion and coextrusion, forging, stamping, rolling, etc., all lead to molecular orientation and resulting high strength in uniaxial or planar directions; the tensile modulus of solid state extruded polyethylene fiber is higher than that of carbon steel.

As evidenced by the contents of this issue, the RETEC program reflected these realities. It was interesting to see that most of the presentations on specific engineering resins turned out to discuss alloys, blends, and composites based on the resin—this is the contemporary industrial reality. As the technical program chairman I wish to express my thanks to all the RETEC speakers. In particular, the excellent review presentations by Prof. R. T. Woodhams and Prof. R. S. Porter contributed greatly to the success of the meeting and were greatly appreciated by all.

L. A. Utracki
Guest Editor

History and Development of Engineering Resins

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A brief perspective of the history and development of the plastics industry is outlined with special reference to engineering plastics and high performance resins. Since the birth of the synthetic plastics industry just over half a century ago, a myriad of polymeric structures have been created of which only a few generic types have attained commercial status. These basic resin types are combined in many ways as composites or blends to make available to industry over 6000 grades for use in fibers, films, coatings, adhesives, or molded shapes. Although plastics are characterized by their mechanical, electrical, chemical, or physical properties, it is their selling price that tends to dominate the volume production of each resin. Today, the modern plastics engineer employs remote-access interactive computer databanks to conduct design and feasibility studies employing the full inventory of resin grades in his assessment. A final section reveals current attempts by researchers to impart extraordinary strength and modulus to conventional plastics by means of solid phase processing, whereby polymeric chains are uncoiled and aligned to produce remarkably tough materials which are likely to challenge the supremacy of steel.

INTRODUCTION

It is generally accepted that plastics materials fall into three major categories referred to as commodity plastics, engineering plastics, and specialty plastics. The commodity plastics are those plastics that constitute the greatest volume of usage, which may individually exceed a rate of consumption greater than one million tons per year on a global scale and includes the polyolefins, poly(vinyl chloride), polystyrenes, and phenolics. Such resins constitute more than two thirds of all plastics consumed. Engineering plastics have been defined by McQuiston (1) as those plastics that possess "high performance" engineering properties, may be processed by conventional methods, and are individually consumed at a global rate exceeding one thousand tons per year. Thus specialty plastics constitute the remaining group, with an annual global consumption less than 1000 metric tons. Since the term "high performance" can have many interpretations depending upon the point of view, in the context of this survey the engineering plastics are subdivided into low, medium, and high performance in relation to the particular property under consideration, i.e., mechanical properties, heat resistance, chemical resistance, or electrical performance. These properties and performance characteristics may be found in numerous handbooks and in the technical literature. *The Modern Plastics Encyclopedia* and its supplement, *Guide to Plastics*, rep-

resent one handy source of information (2), whereas the General Electric Engineering Resins Information System (ERIS) offers designers and engineers a comprehensive remote access data bank for up-to-date comparative information on commercial resins (3). The history of the development of engineering resins has been recently reviewed by Brydson (4). At the turn of the century, only a few plastics materials existed, mainly shellac, gutta percha, and celluloid. Of those only bitumen remains in widespread use. Still the largest volume thermoplastic consumed, approximately 70 million tons of bitumen were used in 1980. Perhaps the first noteworthy synthetic plastics material was that of Leo Hendrik Baekeland who in 1907 developed techniques for the industrial production of phenolic resins. These forerunners were quickly followed by other formaldehyde based resins, the urea and melamine resins now classed as amino resins.

The evolution of the vinyl plastics industry began in Germany about 1930 with the introduction of two important plastics, poly(vinyl chloride) (PVC) and polystyrene (PS), two of the major commodity resins in use today.

In this same period, Fawcett and Gibson (5) of Imperial Chemistry Industry (ICI) in the U.K. made their now famous accidental discovery of the polymerization of polyethylene at high pressure, about 300 MPa. The first polyethylene plant was subsequently commissioned in 1939.

The advent of the Second World War (1939-45)

saw the further introduction of synthetic elastomers as substitutes for the strategically important natural rubber and also the appearance of the copolymer of acrylonitrile-butadiene-styrene (ABS), the first of the rubber-modified plastics materials. This unique method of toughening has now been extended to many other thermoplastics and thermosets including poly(vinyl chloride), acetals, polyesters, epoxy resins, polypropylenes, and polycarbonates. The particle size of the disperse rubber phase is carefully controlled in order to maximize crazing and the related toughening influence on such brittle matrix resins (6).

The first nylon moldings were produced in 1941, but although the fiber form was an instant success (due to the war-induced shortage of silk stockings) the use of nylon 6/6 as a molding resin did not begin to assert itself until about 1950. Today the most widely used nylon engineering resins comprise nylon 6, nylon 6/6, nylon 6/9, nylon 6/10, nylon 6/12, nylon 11, and nylon 12 plus several alloy mixtures of these basic structures representing more than 626 currently available grades (1). Added to this array is another recent entry by Dutch State Mines (DSM) of The Netherlands which has announced commercial plans to produce nylon 4/6, a nylon which has a melting transition near 300°C, only 40°C below its thermal degradation temperature (7). The increased melting temperature and degree of crystallinity of nylon 4/6 imparts greater stiffness, tensile strength, fracture toughness, and heat deflection temperature than other aliphatic nylons. The aromatic nylons (aramids) were introduced in the mid-1960s but these resins did not receive much recognition until the advent of Kevlar fibers. Commercial development of the urethanes began in Germany in 1942 after attempts to circumvent the Du Pont nylon patents. This period also saw the introduction of epoxy resins and unsaturated polyesters, which are both of great importance in the manufacture of fiber-reinforced plastics.

In 1954 Karl Ziegler and his coworkers at the Max Planck Institute for Coal Research ushered in the era of coordination polymerization, beginning with the low pressure polymerization of ethylene. Simultaneous developments occurred in the United States with the Phillips process and the Standard Oil (Indiana) process, which are still practised today. There quickly followed the commercialization of a series of stereoregular polymers and copolymers of butadiene, isoprene, and 1-olefins, in which Giulio Natta and his team of scientists at the Polytechnic Institute in Milan played a leading role in the structural characterization and control of tacticity in this new family of polymers. The outstanding contributions of Karl Ziegler and Giulio Natta to the chemistry of coordination polymerization were recognized when those two scientists jointly received the Nobel Prize for Chemistry in 1960. These Ziegler-Natta catalysts were soon found capable of producing high molecular weight crystalline polymers from propylene. One of these stereoregular polymers, named isotactic polypropyl-

ene, found rapid acceptance. Growth of this stereoregular polymer was so rapid that today it is one of the leading commodity resins. Isotactic polybutene and isotactic poly(4-methylpent-1-ene) were also manufactured with Ziegler-Natta catalysts, but their current volume of usage is still relatively small by comparison. Polyethylene and polypropylene currently comprise nearly half of all the synthetic plastics produced worldwide.

The first commercially available acetal resin produced from formaldehyde was marketed by Du Pont in 1959 under the Delrin tradename. This Du Pont monopoly was shortlived when the Celanese Corporation quickly followed with their acetal copolymer known as Celcon the following year. The combined production of the acetal resins now exceeds 200,000 tons annually.

In 1965 the General Electric Co. introduced poly-(2,6-dimethyl-1,4-phenylene oxide), which is commonly (although incorrectly) referred to as polyphenylene oxide (PPO). This important engineering plastic was synthesized through an unusual oxidative coupling reaction by Hay, Blanchard, Endres, and Eustance (8). In order to facilitate processing of the melt, commercial grades of poly-(2,6-dimethyl-1,4-phenylene oxide) generally contain polystyrene. A few years later, General Electric Co. introduced the polycarbonate (PC) resins almost simultaneously with their introduction by Farbenfabriken Bayer Ltd. in Germany. These tough resins were noteworthy for their unusual clarity, high modulus, and ductility.

After numerous attempts by polymer chemists to develop a superior heat-resistant plastic, the polyimide resin class finally emerged in 1962. Few polymers exceed the high temperature performance of the polyimides, and despite their high cost they have achieved extensive use in demanding applications.

The recent introduction of the polyetheretherketones (PEEK) by ICI in 1977 offered an even greater degree of thermal stability and mechanical property excellence.

The polysulfones were simultaneously developed in the laboratories of Union Carbide Corporation, Minnesota Mining and Manufacturing Corporation (3M), and the Imperial Chemical Industries (ICI). In 1965 Union Carbide introduced their Udel polysulfone resins, which were soon followed by 3M's Astral polyarylsulfones and ICI's polyethersulfones.

In 1967 a patent was issued to Edmunds and Hill of the Phillips Petroleum Company (9) for a new synthesis of polyphenylene sulfide. Commercial production of Ryton polyphenylene sulfide (PPS) began in 1972.

Although the aromatic polyester resins were the subject of extensive investigations beginning with the classic studies of Carrothers, the difficulties encountered in attempts to injection mold poly(ethylene terephthalate) (PET) prevented their commercial introduction until 1966 when AKZO introduced Arnite PETP. The expiration of the basic poly(ethylene terephthalate) patents in 1970 provided the incentive to promote the manufacture of

poly(butylene terephthalate) (PBT) by other companies so that today the combined production of PET and PBT in North America exceeds 30,000 tons per annum. The growth of PET has been particularly rapid due to its application as a packaging material for carbonated beverages.

Table 1 lists some of the more important engineering resins used today and their year of introduction. Although the introduction of new commercial species has begun to subside, the number of available grades, alloys, and modifications of existing polymers continues to proliferate so that more than 6000 grades are currently listed for all plastics. The growth rate for all synthetic plastics materials in the United States beginning in 1930 is plotted in Fig. 1 in relation to the growth of the steel industry. Today the volume production of steel and plastics are nearly equal, which emphasizes the importance of the plastics industry in our economy, an economy that is obviously destined to become ever more dependent upon plastics materials.

According to C. H. Kline (21) there will be an increasing use of polymer alloys such as ABS, modified nylons, polyphenylene oxide/polystyrene blends, and polypropylene/EPDM blends. These four alloys comprise 84 percent of current alloy tonnage. The automotive industry, which traditionally has been at the leading edge of new plastics technology as exemplified by sheet molding compounds (SMC) and resin injection molding (RIM), is beginning to utilize thermoplastic alloys in exterior body panels (Fig. 2), further eroding the position of steel.

The history of the development of engineering plastics reveals only a small part of the total picture

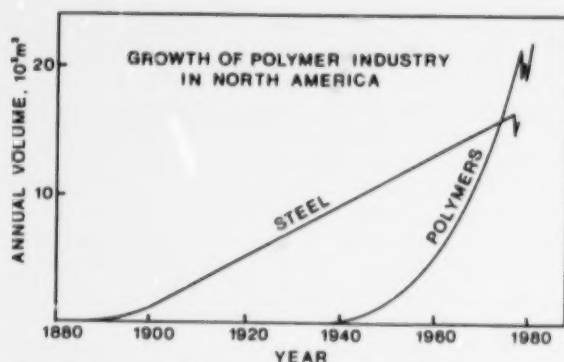


Fig. 1. The remarkable growth of the plastics industry in North America since its inception is compared with that of the steel industry. The growth rate of plastics during the next decade is expected to continue at 7 percent per annum.

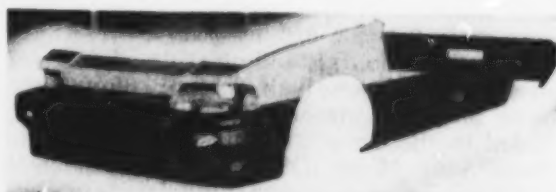


Fig. 2. Thermoplastic body panels for the Honda Civic CRX produced by Kobelco VG, Japan, using Borg Warner Xenoy ABS/polycarbonate alloy.

since there have been many parallel developments in property modifiers, extenders, reinforcing fillers, stabilizers, processing aids, flame retardants, smoke suppressants, coupling agents, colorants, process improvements, and increasingly sophisticated manufacturing technologies related to fabrication and finishing of plastics components. Each resin class has spawned a family of grades tailored for various applications involving differences in composition, molecular weight, formulation or morphology. While it may seem comforting to have such an array of materials available for constructing a particular product, the selection process for determining the most economically attractive engineering plastic can be quite bewildering to the novice. *The Modern Plastics Design Guide* and *ERIS* provide a systematic approach to plastics material selection and design based upon recognized standard procedures (ASTM, UL). Using these procedures the available engineering resins may be ranked with respect to their physical, chemical, electrical, and mechanical characteristics. The following section examines some of the more important design characteristics of the family of engineering plastics.

THERMAL-OXIDATIVE BEHAVIOR OF ENGINEERING PLASTICS

The Underwriters Laboratory (UL) Temperature Index has been recommended as a means of classifying polymer resins according to their long-term durability in air at elevated temperatures. One of the principal characteristics that distinguishes engineering plastics (epoxy, nylon, polycarbonate,

Table 1. Historical Introduction of Engineering Plastics.†

Year Introduced	Resin
1909	Phenolics
1920	Ureas
1927	Poly(vinyl chloride) (PVC)
1930	Polystyrene
1936	Acrylics
1938	Nylons
1939	Melamine-formaldehyde
1939	Polyethylene (high pressure)
1940	Epoxies
1942	Unsaturated polyesters
1943	Silicones
1943	Fluoropolymers
1948	ABS
1954	Urethanes
1954	Polyethylene (low pressure)
1956	Acetals
1957	Polycarbonate (PC)
1957	Polypropylene (isotactic)
1960	Aramids
1964	Polyimides
1964	Polyphenylene oxide (PPO)
1964	Ionomers
1965	Poly(4-methylpentene-1)
1965	Thermoplastic polyesters
1965	Polysulfone
1968	Poly(phenylene sulfide) (PPS)
1978	Polyetheretherketones (PEEK)

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polyester, etc.) from other plastics is their performance at elevated temperatures. The softening temperature of an organic polymer is largely dependent upon the interchain attraction forces attributable to van der Waals or polar interactions between neighboring chain segments. These relatively weak attraction forces are readily overpowered by externally applied stresses or random thermal kinetic motions of the polymer chain. The maximum resistance of the plastic material to creep or flow at elevated temperatures is normally a compromise between the upper limit of oxidative and thermal stability of the polymeric chain and the ability of the resin to be molded. To achieve maximum elevated temperature performance (as in the example of the polyimides or polyetheretherketones) the chain segments must be resistant to both thermal scission (cracking) and air oxidation at processing temperatures, properties which are related to the individual bond dissociation energies as shown in Table 2. These average bond dissociation energies will depend to some extent upon neighboring substituents. Chain stiffness is an additional parameter which the polymer chemist employs to control the softening temperature and modulus of a polymeric resin. Aromatic chain segments may be conveniently employed to increase chain stiffness, whereas ether groups may be used to impart greater chain flexibility (i.e., reduced softening temperature). Some of the more common structural units found in engineering plastics are illustrated in Fig. 3. From the creative efforts of many organic polymer chemists, a spectrum of engineering resins has been developed having the UL Temperature Index Ratings shown in Table 3. These ratings predict the temperature at which 50 percent of the measured property (tensile strength, toughness, or dielectric strength) will be retained after 11,000 hours exposure under static conditions. The polyetheretherketones, polyimides, and poly(phenylene sulfides) are near the maximum temperature limit for organic polymers.

FRACTURE TOUGHNESS

The relative brittle nature of many plastics, particularly when filled, has encouraged numerous attempts to selectively increase the toughness of resin systems without sacrificing other desired properties such as strength, modulus, and heat deflection temperature. Simple plasticization is not always a satisfactory approach for increasing the toughness. It was recognized in the late 1940s that glassy polymers such as polystyrene and SAN could be tough-

Table 2. Bond Dissociation Energies.

Bond	Dissociation Energy kJ/mol
C-F	490
Si-O	450
C-H	410
C-O	360
C-C	350
C-N	310
C-S	270

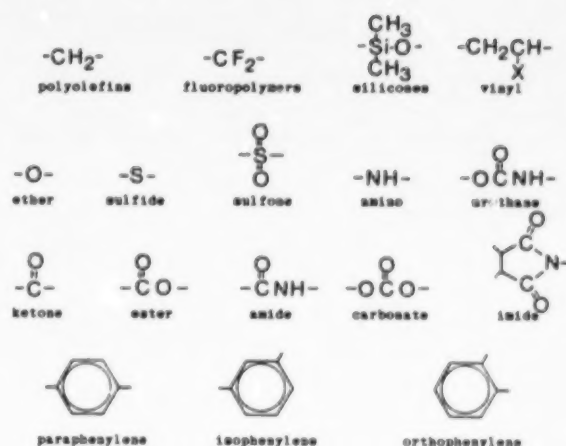


Figure 3. Common polymer chain segments in plastics materials.

Fig. 3. Common polymer chain segments in plastics materials.

Table 3. UL Temperature Index Ratings (2).

	(Degrees Celsius)
Polyetheretherketones (PEEK)	220
Polyimide	200-210
Poly(phenylene sulfide) (PPS)	200-240
Fluoropolymers	150-180
Polysulfones	140-170
Silicones	105-260
Phenolics and Melamines	150
Epoxy	130-180
Unsaturated Polyesters	130
Thermoplastics Polyesters (PET, PBT)	130
Ureas	100
Polycarbonate	100-125
Nylons	65-120
Poly(phenylene oxide) (PPO)	50-105
Polypropylene (PP)	80-120
Acetals	50-95
Polystyrene, SAN, ABS	50
Vinyls	50
Polyethylene	50

ened by the incorporation of tiny, discrete rubber particles which promoted energy absorption through a crazing phenomena (Fig. 4).

Today, many engineering resins use this technique to selectively increase toughness without significantly affecting the modulus and strength. Instead of rubber particles, soft waxy materials such as polyethylene may be similarly employed with equal effectiveness provided that they are adequately dispersed in the matrix phase. Thus the list of plastics toughened by heterogeneous craze nucleation continues to grow and includes thermosetting resins such as phenolics, epoxies, and polyesters as well as thermoplastics such as PVC, nylon, acetals, thermoplastic polyesters, polypropylene, and polycarbonates. Recent evidence discloses that the conditions for crazing are exceptionally critical and demand special attention to the dimensions of the disperse phase (6). Maximum toughness is usually attainable at particle sizes near one micron, although the optimum diameter can be less than 0.1 micron depending upon the crazing behavior of the particular matrix resin. This phenomenon has

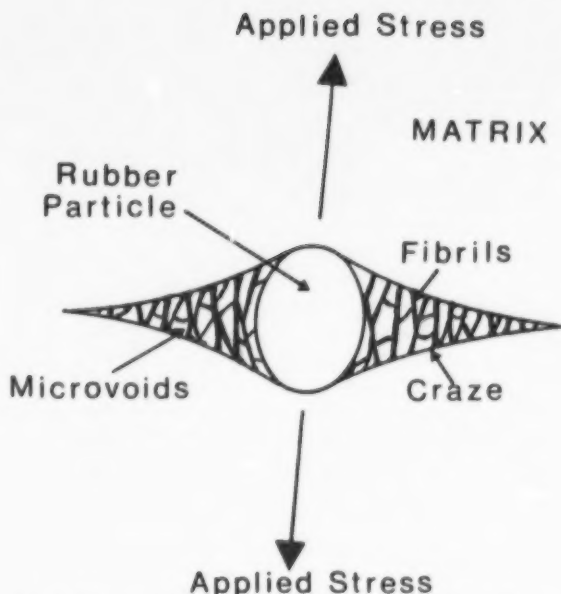


Fig. 4. Microscopic rubber particles impart increased fracture toughness to brittle resins by a process of crazing.

recently been extended by Mathur (10) and Radosta (11) to filled thermoplastics in which the micron-sized filler particles are encapsulated by a suitable organic layer in order to promote the crazing action necessary for toughening. The difficulty in controlling the degree of dispersion and the particle dimensions of the disperse phase is also reflected in the patent literature (12). Many additives are now commercially available for increasing the fracture toughness of brittle plastics.

FLAMMABILITY OF ENGINEERING PLASTICS

The history of plastics materials has been marred by periodic disasters attributable to the flammable nature of most organic polymers, which too frequently cause serious fires and fatalities. It may be recalled that the early celluloid photographic film materials were sometimes accidentally ignited by carbon arc projectors and thereby gutted many theatres before a less combustible cellulose acetate substitute film was finally introduced. Today, flame retardants and smoke suppressants are widely used to reduce the combustible nature of plastics. Although the use of such additives do inhibit combustion, they sometimes increase the formation of toxic gases so that the hazard may actually be increased. The National Bureau of Standards has recently released test methods for assessing the acute inhalation toxicity of combustion products, methods intended for research and screening purposes only. The adoption of such standards is still controversial and it may be several years before a universally accepted test procedure becomes established.

The incineration of plastics waste has also been cited as a potential source of toxic air emissions in urban environments, causing concern about genetic or chronic disorders in humans and other life forms

exposed to these residual toxins. Clearly, more thoughtful consideration must be applied to waste disposal by incineration to avoid permanently contaminating our environment.

MECHANICAL PROPERTIES OF ENGINEERING PLASTICS

The selection of an engineering plastic for a specific application may require that as many as 20 or more individual long-term and short-term chemical, physical, mechanical, and electrical specifications must be satisfied. Usually the short-term mechanical properties are most easily assessed so that such values are commonly employed for initial screening purposes. Long-term performance evaluation may require determination of the creep properties and it has become common practice to refer to creep tables as part of the design process. Examples of these screening methods are described in the published literature (2).

Since engineering resins are often combined with reinforcing fillers, such as glass fibers, to increase their strength, moduli, fracture toughness, and heat deflection temperatures (HDT), it is of interest to rank these composites in order of their load bearing abilities as shown in Table 4. Note that the glass fiber content varies according to the source of information, so that the balance of properties reflect to some extent the quantity of glass fibers which has been incorporated. No clear pattern is evident until this data is analyzed for weight efficiency in terms of flexural stiffness and bending strength for equal mass, a common method of evaluating material performance for automotive applications. The

relative strength $\left(\frac{\sqrt{\sigma}}{\rho}\right)$ and relative stiffness $\left(\frac{\sqrt{E}}{\rho}\right)$

for beams of equal mass are compared for several reinforced thermoplastics in Table 5, wherein the flexural strength (σ), flexural modulus (E), and density (ρ) are used to calculate the performance of a rectangular beam in a three-point bending mode. It is of interest to note that the glass fiber reinforcement does not significantly decrease the weight for equivalent strength or stiffness since the greater density of the inorganic component (glass) offsets the gain in stiffness or strength. With minor differences, these eleven engineering plastics shown in Table 5 are nearly equivalent in terms of bending efficiencies. It is evident that many different plastics may satisfy the mechanical requirements for a particular application. Note that the reinforced isotactic polypropylene ranks near the top in performance on this scale, which makes this material a favored candidate for automotive applications especially in view of its minimum cost compared with other resins. The substitution of mica or talc fillers for the glass fiber component further aids cost reduction with only a minor sacrifice in efficiency (11). Note in Fig. 5 that resin cost still plays a major role in materials selection, an observation which is evident from the volume consumption of a particular resin and its selling price (1980 values); this

Table 4. Mechanical Properties of Glass Fiber-Filled Thermoplastics.

Resin	Glass Fiber Content %	Density g/cm ³	Tensile Yield Strength MPa	Flexural Modulus GPa	Elongation %	Notched Izod J/m	HDT at 1825 Pa °C
PEEK	30	1.51	162	8.7	3	144	312
Polyetherimide	30	1.50	169	8.6	4	107	215
Polyarylsulfone	30	1.37	131	8.5	3	107	204
PPS	40	1.65	134	11.7	3	75	260
PET	40	1.65	159	9	3	107	216
PPO	30	1.57	128	7.9	4	107	158
PC	30	1.4	131	7.6	4	107	146
Acetal	25	1.61	128	7.6	3	96	157
Nylon 66†	40	1.47	138	6.2	4	150	260
PP	40	1.23	103	6.9	3	107	154
ABS	20	1.22	97	4.93	64	104	

‡ Values sensitive to humidity.

Table 5. Bending Efficiencies.

Resin	Glass Fiber Content %	Strength	Stiffness
		$\frac{\sqrt{\sigma}}{\rho}$	$\frac{^3\sqrt{E}}{\rho}$
		ρ	ρ
PEEK	30	8.4	1.36
Polyetherimide	30	8.6	1.36
Polyarylsulfone	30	8.3	1.49
PPS	40	7.0	1.37
PET	40	7.6	1.26
PPO	30	7.2	1.26
PC	30	8.1	1.40
Acetal	25	7.0	1.22
Nylon 66	40	8.0	1.24
PP	40	8.2	1.54
ABS	20	8.0	1.39

quently a fully extended polyethylene chain should possess tensile strength values near 30 GPa with an ultimate elongation of 34 percent (13). Recent advances in polymer technology have demonstrated that such large increases in the modulus and strength of polyethylene may in fact be obtained by a gel spinning process followed by ultradrawing (14, 15). These superstrong polyethylene fibers possess tensile strength values near 4 GPa and a Young's modulus approaching 220 GPa. On a weight basis, such fibers exceed the specific properties of steel, carbon fibers, and aramid fibers. I. M. Ward (16) has pointed out that there are two essentially different approaches to the production of highly oriented chain structures:

- The synthesis of polymer chains that are inherently rigid extended-chain rod-like molecules, or
- Superdrawing processes under conditions of very large plastic deformation that simultaneously unfold and orient the polymeric chains so that they retain their extended configurations in the solid state.

The first breakthrough in the development of highly oriented polymers owed its success to the preparative skills of the Du Pont polymer chemists who first synthesized rod-like molecules from aromatic polyamides (aramids). These solution spun molecules gave rise to the remarkable Kevlar fibers with their characteristic high strength (2.8 GPa) and Young's modulus intermediate between that of aluminum and steel (124 GPa). Commercial production of the aramid fibers began in 1972 and since then their use has increased dramatically.

The second breakthrough arose out of the extrusion studies of Southern and Porter (17) in 1969 who demonstrated that ultrahigh modulus fibers of polyethylene could be produced by high pressure extrusion of polyethylene near its melting point through a capillary die with a very large reduction ratio. Further improvements in the method of manufacture were reported by Coates and Ward, in 1981, who coupled the solid phase extrusion process with simultaneous drawing of the extruded filament from the die. Other fringe benefits included reduced permeability (tenfold) and increased thermal conductivity in the draw direction. The solid phase hydrostatic extrusion of polyethylene has

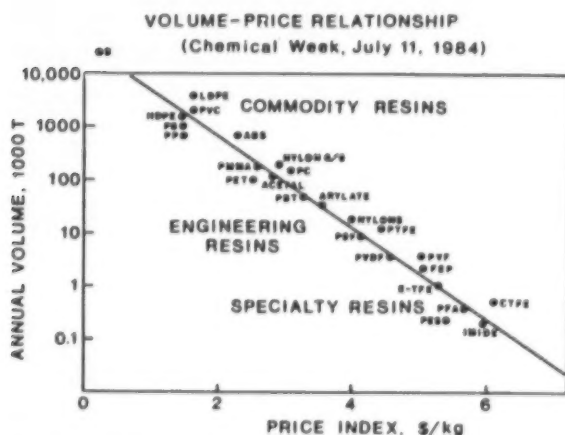


Fig. 5. With few exceptions, the production volume of a plastic material (including steel and aluminum) is governed by price. The lone point (B) in the upper left (off the diagram) is asphaltic bitumen.

observation is also true for asphaltic bitumen, which at 20 cents per kilogram has a global 1984 market near 60 million tons.

SOLID PHASE PROCESSING AND THE SUPERPLASTICS

It has often been noted in the literature that simple carbon-carbon bonds have ultimate strength values of the order of 100 GPa and that conse-

Table 6. Solid Phase Processing of Polyolefins.

	Polyethylene	Polypropylene	Kevlar
Tensile Strength, MPa	26 → 4000	33 → 870	2760
Young's Modulus, GPa	1.0 → 150	1.1 → 20	124
Notched Izod, J/m	81 → 1000+	54 → 1100	—
Elongation, %	100+ → 3.9	100+ → 6	2.5
Melting Point, °C	133 → 150	162 → 170	390 (dec.)
Density, g/cm ³	0.96	0.90	1.44
Stiffness E''	5.5	3.0	3.5
Weight ρ			

been extended to other engineering plastics such as polypropylene, acetal, PEEK, PVDF, nylon, and thermoplastic polyesters. Commercial development of biaxially oriented sheet materials (BeXor) produced by hydrostatic extrusion and suitable for stamping or thermoforming has been announced by Kusan, a division of the Bethlehem Steel Corporation (18). The extraordinary strength and toughness of BeXor sheet materials make them suitable for ballistics shielding, e.g., a 2.5 cm thick BeXor sheet will stop a 38 caliber bullet fired at close range.

Current investigations are focussed on the solid phase rolling and drawing of crystalline polymers to achieve similar chain uncoiling and alignment in sheet materials analogous to the techniques employed by the steel industry with respect to the cold rolling of steel sheet. Dingra, Spruiell, and Clark (19) have related the underlying molecular structure changes during rolling (both unidirectional and biaxial) of polypropylene with the corresponding property modifications. Bigg, Smith, Epstein, and Fiorentino (20) explored the process parameters for high speed rolling of polyethylene and polypropylene tapes and were able to achieve output rates of 12 m/min. This is still far less than the rolling speeds common for steel (up to 1200 m/min) and that of fiber spinning (near 5000 m/min).

These remarkable increases in performance have been summarized in Table 6 and compared to Kevlar. The arrows indicate the maximum observed changes in each property after drawing, rolling, or extruding compared to the original undrawn material. The stiffness per unit mass (in bending) is proportional to the cube root of the modulus divided by the density. This ratio is a qualitative measure of the stiffness efficiency for applications requiring minimum weight (as in aerospace and transportation). Such large increases portend the development of a whole new spectrum of self-reinforced thermoplastic sheet materials greatly exceeding the performance levels of today's engineering resins and suitable for a broad range of applications including housing, transportation, food packaging, electronics, marine, and general construction.

The history of engineering plastics is now on the verge of entering its most exciting phase—the Age of Superplastics—which will offer special new opportunities for growth and development in some areas, while further eroding the use of our traditional materials of construction—wood, steel, and glass. The wise entrepreneur will view the full spectrum of plastics as his stable for the future, and by proper application of the available design data, select the appropriate resin for each task according to proven systematic guidelines.

REFERENCES

1. H. McQuiston, *Plast. Eng.*, **57**, 18 (1980).
2. "Modern Plastics," McGraw Hill Publication Co., P.O. Box 430, Hightstown, NJ 08520.
3. General Electric Co., Plastics Operations, 1 Plastics Avenue, Pittsfield, MA 01201.
4. J. A. Brydson, "Plastics Materials," 4th Ed., Butterworth Scientific (1982).
5. E. W. Fawcett and R. O. Gibson, *Brit. Pat.* 471,590 (Sept. 6, 1937).
6. B. Z. Jang, *SPE ANTEC Tech. Papers*, **30**, 523 (1984).
7. D. A. O'Sullivan, *Chem. Eng. News*, **62**, No. 19, 19 (1984).
8. A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, *J. Am. Chem. Soc.*, **81**, 6335 (1959).
9. J. T. Edmunds and H. W. Hill, *U.S. Pat.* 3,354,129 (Nov. 1967).
10. K. K. Mathur and S. B. Driscoll, *J. Vinyl Technol.*, **4**, 81 (1982).
11. J. A. Radosta, *SPE ANTEC Tech. Papers*, **30**, 145 (1984).
12. J. F. Ross, *U.S. Pat.* 4,375,531 (March 1, 1983).
13. H. Mark, *Ultimate Properties of Polymers*, ACS Division of Colloid and Surface Chemistry, Kendall Award Symposium, New York City, April 5-8, 1976.
14. S. Kavesh and D. C. Prevorsek, *U.S. Pat.* 4,413,110 (Nov. 1, 1983).
15. P. L. Lemstra and P. Smith, *J. Mater. Sci.*, **15**, 505 (1980).
16. I. M. Ward, *Physics Bulletin*, p. 66, (Feb. 1977).
17. J. Southern and R. S. Porter, *Am. Chem. Soc., Div. Polym. Chem. Polym. Prepr.*, **10**, 1028 (1969).
18. A. R. Austen, D. V. Humphries, and C. L. Fay, *SPE ANTEC Tech. Papers*, **28**, 837 (1982).
19. V. J. Dingra, J. E. Spruiell, and E. S. Clark, *Polym. Eng. Sci.*, **21**, 1063 (1981).
20. D. M. Bigg, E. G. Smith, M. M. Epstein, and R. J. Fiorentino, *SPE ANTEC Tech. Papers*, **28**, 74 (1982).
21. C. H. Kline, *Chemical Week*, p. 31, (May 2, 1984).

Thermoplastic Polyester Resins For Containers

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An overview of the use of polyesters for containers is presented. The market for polyethylene terephthalate container resin should reach 760 million pounds by 1989. Diethylene glycol, a polymerization by-product, and other comonomers reduce the polymer melting point and crystallization tendency, yielding wider container processing latitude. The effect of these modifications on creep and tensile strength is discussed. Improved gaseous barrier approaches and hot-fillable container opportunities are presented. Newer applications for thermoplastic polyester containers are summarized.

THERMOPLASTIC POLYESTER RESINS FOR CONTAINERS

The commercial use of poly (ethylene terephthalate) (PET) for films and textile and industrial yarns (including tire cord) has been highly successful for many years. More recently PET's combination of high strength potential, light weight, excellent color and transparency, and safe toxicology, has led to its acceptability for manufacture of food-stuff containers.

This overview of thermoplastic polyester resins for containers addresses developments and the current status of PET and slightly modified copolyesters having properties similar to PET. This paper presents PET's market potential, the chemistry and manufacture of container resins, production of containers and their performance characteristics, newer resin developments, and some of the emerging applications for PET.

Goodyear introduced PET resin for carbonated beverage containers in 1977 and that initial market of 22 MM pounds has grown rapidly to 515 MM pounds in the U.S. by the end of 1983. The 2 liter bottle accounted for 75 percent of this total. This growth was mirrored in Europe (mainly the U.K.) starting a few years later and amounted to about 90 MM pounds of resin in 1983. Expansion of PET carbonated beverage containers into Ontario is imminent, although markets already exist in other provinces. The USA market for container resins is forecast to reach 760 MM pounds by 1989, representing an average growth rate of 6.3 percent. The use of PET for containers is spreading rapidly and may be truly considered to be a world-wide market.

CHEMISTRY AND MANUFACTURE OF PET

Prior to discussing why PET has been so widely accepted for container applications it is important

to understand the chemistry and resin manufacturing processes involved. There are two different routes to commercial PET, based on the starting terephthalate monomers used. Either dimethyl terephthalate (DMT) or terephthalic acid (TPA) is reacted with ethylene glycol (EG) to yield a first stage product. In the DMT process the effective monomer, bis (hydroxyethyl) terephthalate (bis HET) is first formed by the catalyzed transesterification of DMT with two equivalents of EG. In contrast in the TPA process, the esterification reaction is self-catalyzed by the carboxyl group acidity. Apart from not requiring a first stage catalyst, the initial esterification product is a low molecular weight mixture of PET oligomers.

The final process involves polycondensing at elevated temperatures and high vacuum in the presence of a metallic catalyst (usually an antimony compound). The polycondensation process involves both esterification and ester-interchange reactions, with removal of water and EG. Polyester chemistry involves reversible reactions necessitating removal of methanol, water, and EG to increase the molecular weight to the desired level. The molten mass of PET is then extruded from the reactor, quenched rapidly with water cooling and pelletized to small resin particles (~2.5 to 3.5 mm cube).

These pellets are further polycondensed in a solid state polymerization reactor operating at a safe temperature below the melting point of PET. In the solid state polymerization process the initially amorphous, transparent pellets are thermally crystallized, increase in density (1.335--1.400 g/cc) and turn opaque. The number average molecular weight (M_n) used for most containers (e.g. carbonated beverages) ranges from 24,000 to 31,000, or intrinsic viscosities of 0.70 to 0.85, respectively. The melt viscosities at 280°C and zero shear for these two molecular weights are approximately

5000 and 13,500 poises, respectively. Some specialized container applications require a resin IV of 1.0 ($M_n \sim 40,000$) having a zero shear melt viscosity at 280°C of approximately 30,000 poises.

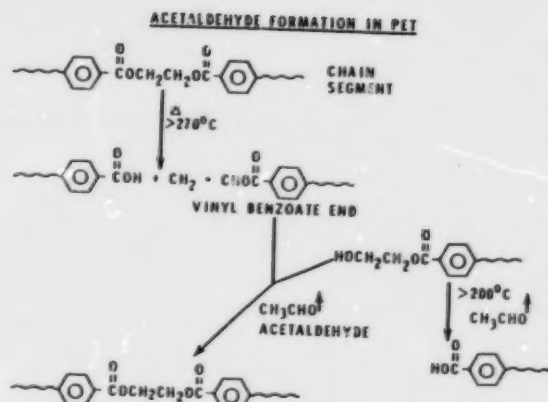
Two by-products during the production of PET are diethylene glycol (DEG) and acetaldehyde (AA). DEG is an ether-containing glycol incorporated in the polyester chain. The DEG is effectively a comonomer glycol, which reduces the melting point of the PET resin proportional to the amount incorporated in the structure. Higher levels of DEG, therefore, permit lower extruder temperatures during molding operations. The incorporation of DEG also interrupts the regularity of the PET morphology and reduces the crystallization tendency of resin. The modulus potential after orientation and glass transition temperature (T_g) also are lowered with increasing DEG content, and consequently pressurized containers will exhibit increased tendency for creep, especially at high ambient temperature exposures.

Acetaldehyde (AA), which affects the taste of carbonated cola beverages at a 60 parts per billion level, is present in all PET resins. It is produced by thermal decomposition of hydroxyl end-groups at temperatures greater than 200°C or their interaction with the primary vinyl benzoate from ester bond thermal scissions (1) in the melt as shown in Fig. 1. Thus, all PET resin melts contain a certain amount of AA. Although AA boils at 21°C, it has sufficient solubility in PET in addition to the melt viscosity retardation influence, that parts per million quantities (30 to 150 ppm) are entrapped in the pelletized resin. The routes shown for AA formation illustrate that whenever the necessary thermal conditions exist it will be generated, emphasizing the need to minimize molding temperatures and extruder residence times to achieve low AA content in PET containers.

PET CONTAINER MANUFACTURE

Before discussing the manufacture of PET containers a brief review of PET's pertinent properties improves understanding of the processes involved. The key thermal transitions of amorphous PET as it is heated from ambient conditions are its glass transition temperature ($T_g \sim 70$ to 80°C), onset of crystallization ($\sim 120^\circ\text{C}$), and the melting point (~ 250 to 260°C). Orientation of containers by blowmolding is usually conducted at temperatures above the T_g but below crystallization onset temperatures. The relationship between crystallization rate and temperature is defined by a U-shaped curve, depending on the resin composition (Fig. 2). It may be seen that PET crystallizes most rapidly in the 160 to 180°C range and that rapid cooling from the melt is required to obtain amorphous parts. Also higher molecular weight resins crystallize more slowly than lower ones.

The highest volume usage of PET is currently for biaxially oriented carbonated beverage bottles. However, the strength development observed in these is also applicable to other thin wall nonpres-



CRYSTALLIZATION RATE OF PET (CLEARTUF® 7207)

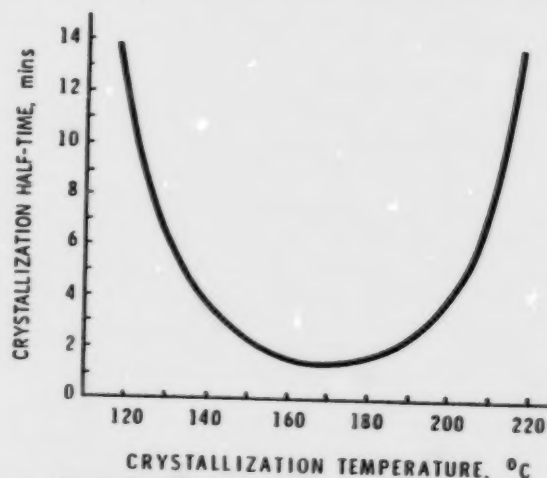


Fig. 2. Crystallization rate of PET (Cleartuf® 7207).

surized containers requiring a balance of strength, light weight, and transparency. Two basic processes are in current use (1) one-step or in-line, and (2) two-step or reheat blow (RHB). Greater overall production rates are achieved with the RHB process equipment, involving injection molding an amorphous preform and then reheating it to the preferred temperature for orientation by blowmolding. The injection and blowmolding are carried out in separate equipment. The one-step method forms the preform and blowmolds in the same equipment and reaches the preferred orientation temperature by carefully controlled cooling from the molten state. The preform exiting the injection mold is hotter than its counterpart in the RHB process. In both cases rigorous drying to less than 50 ppm moisture content is required immediately prior to injection molding to minimize hydrolytic degradation. It is important that dried resin is not allowed to regain moisture. Detrimental levels may be reached within seconds, depending on the humidity exposure. Hopper driers positioned directly above the injection molding extruder are essential for

maximum retention of molecular weight. The amount of effective orientation achieved in the final bottle depends on the dimensions of the preform and the blowmolding conditions. The preform is usually designed to approach the preferred 2 to 1 hoop:axial strength ratios for a pressure vessel. Normally area stretch ratios of the outer and inner surfaces between preform and 2 liter bottle are 10-to-1 and 13-to-1, respectively, with outer and inner hoop stretch ratios of 3.7 and 4.7, respectively.

In the RHB process if the preform is too cold at the point of blowmolding an objectionable haze or pearlescence, arising from the presence of microvoids, is seen. On the other hand, if the preform is too hot opacity arises from the production of spherulitic crystallites. Between these two temperature extremes at approximately 100°C, visually acceptable bottles are obtained, and this range defines the "process window". Typical injection and blowmolding conditions used in our lab equipment are shown in Table 1. The preform is heated to blowing temperatures using Calrod heaters, whereas most commercial equipment uses quartz radiation near infra red centered at 1.3 micron wavelength for faster, more uniform heating. The injection and blowmolding conditions used will vary depending on the resin composition and molecular weight, heating and stretch ratios involved, and equipment characteristics.

Apart from many physical, thermal stability, and appearance requirements, specifications generally direct that 2 liter bottles for cola beverages must not exceed 3 µg of AA per liter of bottle headspace, when stored at 70°F for 24 hours. A typical AA content from resin through the molding process to the preform for acceptable bottle headspace values is shown in Fig. 3. The amount of AA generated in injection molding increases rapidly, as expected for a chemical reaction, under the influence of higher temperatures and residence times. Thus, the AA headspace value readily indicates the thermal exposure condition and the uniformity of the injection molding process. Blowmolding has a minor influence (reduction) on the eventual bottle headspace

TYPICAL ACETALDEHYDE HISTORY THROUGH DRYING AND INJECTION

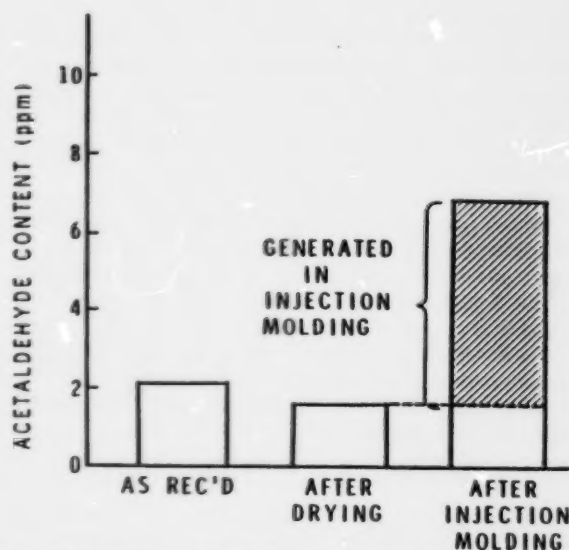


Fig. 3. Typical acetaldehyde history—through drying and injection.

value, since no additional AA is generated at the temperatures involved.

PET RESIN DEVELOPMENTS

The two liter PET bottle which initially weighed 60 to 70 g has now been lightweighted in stages to ~50 g currently to improve economics. This has generally been achieved by changes in design involving shorter, thicker preforms with higher stretch ratios in the final bottle. Increased productivity demands, requiring faster injection and blowmolding cycles, exceeded the capabilities of the first generation polyester container resins. This competitiveness led to the development of improved clarity PET resins with lower melting points (4 to 6°C) and reduced tendency to crystallize. The lower melting point permits lower extruder temperatures and gives the potential for lower AA in bottle headspace. The RHB process window was also widened on the low temperature side, permitting blowing at colder temperatures without haze development. This is possible since the T_g has been slightly reduced with the higher DEG level. The development of crystalline haze occurs at about the same temperature as with the lower DEG composition. Although such resin modifications are useful to the industry, others require even greater modifications. Container resins modified with diacid (isophthalic acid) or diol (cyclohexanedimethanol) comonomers are now offered to the bottle manufacturers. These give a further reduction in melting point (~4 to 15°C) and in crystallization tendency, and also widen the RHB process window on the high temperature side. This permits demolding preforms hotter, and also recycling them through the

Table 1. Injection and Blowmolding of 21 PET Bottle (65 g wt)—Cleartuf® 7207 Resin.

Injection¹	
Extruder Temperature (°C)	277
Mold Cavities	4
Injection Rate (g/sec)	9
Chill Water (°C)	2-5
Cycle Time (secs)	30
Blowmold²	
Mold Cavities	1
Heating Time (secs)	
Oven	107
Equilibration	10
Blowing	3.5
Decompression	2.0
Load—Unload	6
Total cycle	128.5
Blow Pressure (Kg/cm ²)	25
Center Rod Velocity (cm/sec)	30

¹ Cincinnati Milacron 270 Metric Ton.

² Cincinnati Milacron RHB-L.

heating ovens when blowing holdups occur, while still preventing crystalline haze development. Depending on the application, care must be exercised when using the hot end of these wider process windows. It has been observed (2) that both creep (thermal stability) and strength performance are reduced when containers are reheated blown at the higher temperatures, although transparency is retained *Figs. 4 and 5*. The overflow volume increase arising from creep of a carbonated bottle at 38°C for one day is shown in *Fig. 4*.

Containers applications requiring color have available precolored PET resins in emerald green (citric beverages, wine etc), Georgia Green (wine), and amber (liquor, oils etc). Titanium dioxide pigmented resins are also marketed for white applications.

Two desirable improvements in polyester container resins which would considerably extend the market potential are (1) greater gaseous barrier, and (2) hot fillability.

IMPROVED BARRIER POLYESTER

The gaseous barrier properties of PET place it within the class of high barrier amongst all polymers

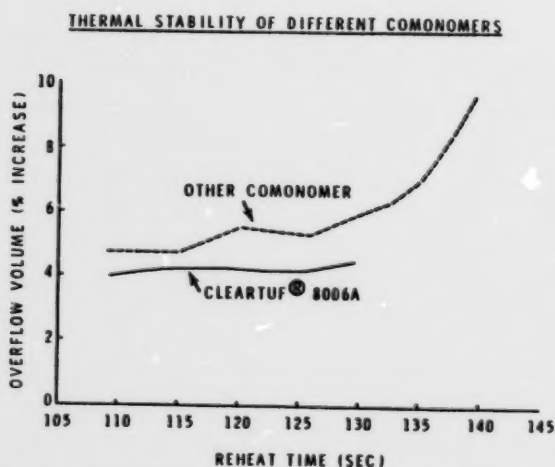


Fig. 4. Thermal stability of different comonomers.

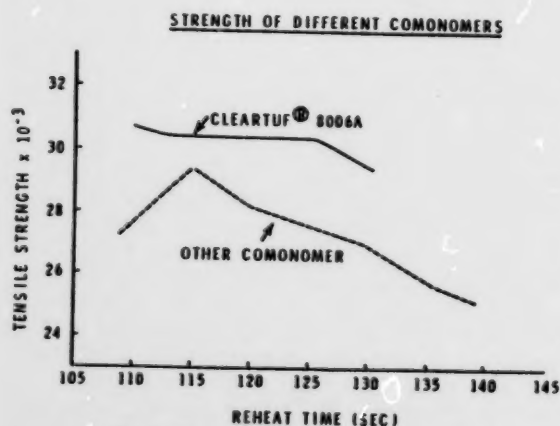


Fig. 5. Strength of different comonomers.

Table 2. However, within this class there are polymers with considerably better oxygen and carbon dioxide barriers than PET. Amongst others, applications requiring improved oxygen barrier include ketchup and beer, whereas better carbonation retention is needed for thin walled small volume containers such as cans and half-liter bottles. Multilayer laminates or coextrudates involving ultra-high barrier resins, e.g. poly(vinylidene dichloride) (PVDC) and poly(ethylene-vinyl alcohol) (e.g. EVAL), are used with lesser barrier materials to yield desired composite container barrier performance. However, such combinations may be costly and present considerable problems when recyclability becomes an important factor. Coated and coextruded containers should always be evaluated on a cost effectiveness basis compared to thicker wall PET containers, where moderate barrier improvements are required.

Polyester compositions are known with improved barrier properties compared to PET. Although three-fold improvements are possible with certain aromatic comonomers, their high cost (>\$2.00 per pound) and high modification level prohibit their usage for current commercial containers. Polyester resin manufacturers are actively pursuing programs to define an improved barrier polymer, but none have produced a commercially available product.

HOT-FILLABLE CONTAINERS

Many foodstuffs require hot-filling in the temperature range 85 to 110°C. Biaxially oriented PET containers are thermally stable only to temperatures of approximately 60 to 65°C (just below the T_g). Thermal shrinkage of PET containers may be improved to permit hot-filling by heat-setting treatments under constraint. Treatments of twenty seconds or less in the temperature range 160 to 220°C are sufficient to yield hot-fillable PET containers. Although oriented regions remain clear after heat-setting, amorphous or slightly oriented areas develop spherulitic crystallites and turn opaque. Nevertheless, acceptable container designs, including ribbed reinforcements to resist deformation (panelling) when subjected to the vacuum created on cooling after a hot-fill, have already been demonstrated in Japan and are expected in the U.S. this year. The technology used for these containers is proprietary, but it is expected that other hot-fillable

Table 2. Oxygen Permeability of Polymers.

Polymer	Oxygen Permeability ¹
20/80 Poly(ethylene/vinylalcohol)	
Dry	0.04
50% Relative Humidity	0.2
Polyacrylonitrile	0.05
30/70 Poly(styrene/acrylonitrile)	1.0
PET	
Oriented/Heat Set	3.0
Amorphous	8.0
HDPE	110
Polycarbonate	250

¹ cc-mil/100 in² Dry Atmosphere 23°C.

containers will follow as equipment capabilities become available. Another route to hot-fillable containers is through use of polyester compositions with higher T_g s than PET. These usually require more rigid comonomers, which may suffer from adverse economics. Thus, improved thermal stability containers can be manufactured from PET by heat-setting involving longer cycle times, or from higher priced polyester compositions. The specific container needs and market economics will determine the preferred route.

RECENT POLYESTER CONTAINER APPLICATIONS

Many new container applications for PET are emerging. Non-beverage containers are in use for wine (emerald and Georgia Green up to 3 and 4 liter sizes), liquor (50 mls up to 1.75 liter), beer (PVDC-coated, in U.K.), food trays (coated paperboard and dual ovenable), pickles (wide-mouth), mouthwash, cough syrups, sleep inducers, cosmetics, and household cleaners (Japan). The dual ovenable trays required the development of faster crystallizing resin compositions (for faster setup) and higher molecular weight (for good cold impact strength) in contrast to carbonated beverage con-

tainers. Generally, the other applications have been achieved using existing commercial resins, including color and molecular weight variations. A recent non-food application which has been successfully introduced in the U.S. is the transparent tennis ball container. This is an offshoot of carbonated beverage technology requiring retention of 82.74 kPa air pressure to ensure good ball playability.

Evaluations are underway for thermoformed cans (with and without heat setting), edible oils, peanut butter, juices, water, pourable and spoonable dressings, and aerosols. We have demonstrated the feasibility of large oriented containers up to 22 gallon size in the laboratory. We have also made prototype fuel tanks and shown acceptable performance on small tractors for both gasoline and diesel fuels, without the need of fluorination treatments used with polyethylene containers.

In summary, the use of PET for containers is firmly established. Current evaluations involving new resins, equipment, and container design are likely to create many new market opportunities for this versatile material.

REFERENCES

1. L. Buxbaum, *Angew. Chem., Int. Ed.*, **7**, 182 (1968).
2. C. L. Kern, *Plast. Eng.*, **40**, 37, (1984).

Polycarbonate Resins

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An outline of the history and manufacture of polycarbonate resins is followed by a discussion about resin product types and their processing. The key properties of flex modulus, deflection temperature, and impact are those that make polycarbonate resins premier engineering resins. Like most other engineering plastics, polycarbonate resins' early commercial history was characterized by substitutions of polycarbonate resins for traditional materials, particularly metal and glass. Examples of applications are presented. More recently application developments involve *ab initio* selection of polycarbonate resins and article designs based on polycarbonate resin properties. In addition, "tailored" resins such as poly(ester carbonate) resins and polycarbonate resin blends have evolved to meet specific applications. The future growth of polycarbonate resins is predicted to feature few new resins, many new blends, and application developments using computer techniques.

INTRODUCTION

Polycarbonate resins (Fig. 1a) based on bisphenol-A (Fig. 1b) are the reference materials of the engineering thermoplastics industry. Resin volumes have grown rapidly with 600 MM lb. of sales projected for 1984. This is a far cry from the first laboratory samples produced by Schnell at Bayer, AG in Germany and Fox at General Electric Company (GE) only 30 years ago (1 to 3).

It is interesting to note that polycarbonate resins became industrial materials as a result of technical discoveries, not because of a perceived marketing need. This contrasts with the growth of polycarbonate resin products and other engineering resins in the succeeding years. Schnell was extending Bayer's polyester patent portfolio, which then emphasized poly(ethylene terephthalate) (PET). Fox, on the other hand, was searching for improved polyester wire enamels. In both cases the semi-aromatic diol bisphenol-A was used as the basis of their aromatic polycarbonate studies. This, too, was a technically happy event. Undoubtedly both workers used the diol because it was readily available, having been used in the epoxy resin industry for some half dozen years. In the intervening time many related bisphenols have been used, but none has achieved the mix of properties, cost, and availability, that the original bisphenol-A contributed (4).

Schnell and Fox's work occurred simultaneously. Who had priority was not certain. Thus the two firms fielded products at about the same time in the late 1950s. Initially Bayer marketed primarily in its

home base Europe and GE emphasized the U.S. market. In the mid-1970s both firms expanded their international activities. GE set up its European operation based in The Netherlands. Bayer is competing in the U.S. through its wholly owned subsidiary Mobay. Other firms, including several in Japan, offer polycarbonate resins. Recently in the United States Dow has been test marketing resin. Bayer and GE are considered the volume leaders.

MANUFACTURE

Both Bayer and GE set up semi-works facilities that came on stream in 1958. Both were based on phosgenation of bisphenol-A. General Electric initially used a solvent process (Fig. 2a) and Bayer used both an interfacial (Fig. 2c) and melt process (Fig. 2b). Both companies have now settled on an interfacial process (5). In an interfacial process the bisphenol-A is dissolved as a disodium salt in aqueous caustic and reacted with phosgene bubbled into a methylene chloride layer. Reaction occurs at the solution's interface with the polymer "growing" into the methylene chloride layer. Chain length is controlled by addition into the reaction mixture of a monohydroxyphenolic compound. The methylene chloride layer is then separated, and the polymer is isolated by removal of solvent (1, 2). Here the various producers have developed a number of different processes, including devolatilization extrusion, granulation, and spray drying.

In devolatilization extrusion a higher boiling solvent may be exchanged for the methylene chloride, concentrated, and run through a vacuum vented

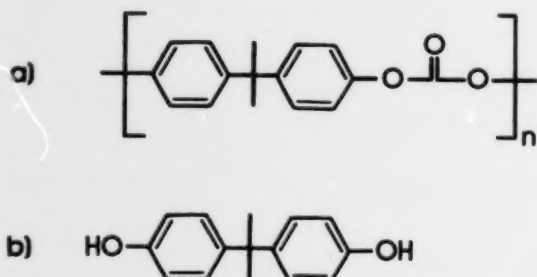


Fig. 1. (a) Polycarbonate resin (PC); (b) Bisphenol-A (BPA).

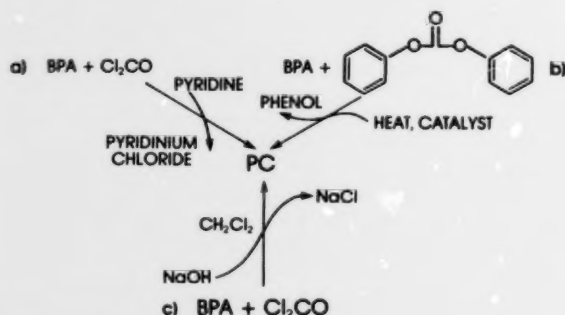


Fig. 2. Polycarbonate resin production processes (a) Solution; (b) Melt; (c) Interfacial.

extruder to form pellets. One type of granulation process introduces the methylene chloride solution into hot water. The solvent boils off and the friable, polycarbonate resin is deposited. After drying, amorphous polycarbonate pellets are formed by extrusion of the granules. Spray drying vaporizes the methylene chloride solvent with concurrent precipitation of powdered polycarbonate resin. The powder is then extruded into pellets or other articles.

PRODUCTS

Polycarbonate resins are produced as colorless, transparent, tinted, pigmented, filled, or glass reinforced pellets for injection molding. In addition, the products can be differentiated by melt viscosity, flame retardancy, and impact modification.

Grades of polycarbonate resin are also available for blowmolding. Here the resin molecules are modified by introducing chain branching to increase the melt strength. This allows the resin to be extruded into a parison with sufficient dimensional integrity so that the mold can close and the resin may be blown.

Polycarbonates may be processed into structural foam. This is done by introduction of an inert gas into the melted resin or decomposition of a chemical blowing agent. In either case the gaseous polycarbonate mixture passes from a high pressure accumulator into a low pressure mold which allows the gas to expand resulting in a porous sponge-like structure.

Polycarbonate resin is sold as sheet and film. These products are used for a wide range of appli-

cations ranging from laminates which are used in "bullet resistant" glazing systems to the hollow core sheet used for greenhouse glazing. The sheet and film can be thermoformed into articles. Typical products include signs, window bubbles, skylights, lighting products, and dishware.

PROPERTIES

Polycarbonate products have steadily made inroads on traditional engineering materials, especially metals and glass. This is due to polycarbonate's property profile, ease of processing, and the ability to design polycarbonate parts multifunctionally.

To be an engineering thermoplastic a material must be formable and maintain dimensional stability and mechanical properties over a wide temperature range (4). Because we live in a world highly influenced by water, the temperature range often used as a benchmark is 0 to 100°C. In Table 1 critical engineering material properties are summarized. The relatively high flex modulus, coupled with impact resistance, makes polycarbonate resins stiff and tough and, hence, appropriate for structural applications. The high deflection temperature insures that the polycarbonate resins will perform well above the boiling point of water.

Most of the polycarbonate resin production is used for injection molded parts. Polycarbonates possess relatively non-Newtonian apparent viscosity versus shear rate profiles at low shear rates. Thus below 1000 s⁻¹ at typical 300°C molding temperature, viscosities in the range of 10,000 Pa·s are maintained, which gives the molten resin sufficient body in the injection molding machine barrel and immediately after injection in the mold cavity. During the high shear injection the resin behaves in a more Newtonian manner and it flows readily during the injection stroke into the mold. Such processability has allowed polycarbonate resin parts of several kilogram sizes to be processed at moderate clamp pressures. Of course with foam grade polycarbonate resins the situation is even more favorable, with the foamed resin expansion assisting in the mold filling process. Here complex parts with edge dimensions over a meter can be readily formed.

The ease of processability also allows parts to be made into almost any shape. Complex assemblies can be reduced from multi-part, multi-step manufacturing sequences to a single plastic part pro-

Table 1. Polycarbonate Resin Properties.

Property (SI Units)	ASTM Test	Value
Deflection Temperature @ 1.82 N/mm ² (°C)	D648	134
Izod Impact, Notched 3.2 mm (J/m)	D256	600-800
Flexural Modulus, Tangent (N/mm ²)	D790	2300
Dielectric Strength in air (KV/mm)	D149	15
Dielectric Constant @ 60-10 ⁶ Hz	D150	3
Transmission (%)	—	88
Processing Temperature (°C)	—	290-320
ΔIV @ 250°C, 16 hr.	—	0.01

duced in a single injection molding step. This results in reduced costs for such assemblies.

As with any material of construction one must be aware of the environmental factors to which a part is subjected. Polycarbonate resins are amorphous polymers, and can be attacked by certain solvents. Ketones and chlorocarbon solvents are especially aggressive. Even gasolines and oils will affect neat polycarbonate resins. Secondary finishing processes such as painting, solvent adhesion, and gluing must be carefully selected.

APPLICATIONS

Polycarbonate resin is filling requirements in many applications ranging from instrument panels in automobiles to football helmets. The magnitude of polycarbonate uses and the variety of specific applications is often surprising. For instance, in the transportation field a typical 747 jumbojet will contain several hundred pounds of polycarbonate resins in everything from food serving devices to windows to wing tip light covers. Table 2 highlights common applications.

RECENT DEVELOPMENTS

As noted in the foregoing, existing polycarbonate resin products are being used in many product areas. We expect that uses for these products will continue to expand, but still more applications can be expected from new polycarbonate technology. Technology now appearing includes new resins, polycarbonate blends, and new concepts in application design, mold design, and prototyping.

The combination of polyester chemical and heat resistance with polycarbonate toughness, clarity, and processability has been achieved in polyester carbonate resins (Fig. 3). Several companies have fielded materials which have pushed polycarbonate resin applications from the polycarbonate 134°C

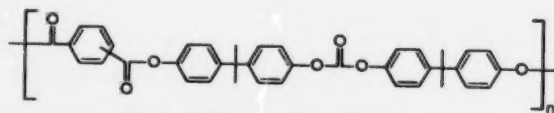


Fig. 3. Polyestercarbonate resins.

HDT to the 164°C level. Thus applications requiring polycarbonate-like properties with enhanced HDT can be served. Such applications include safety items such as firemen's helmets and automotive fuses. Additional chemical resistance allows consideration of autoclavable medical and biological devices.

Blends of polycarbonate resins have also become available within the past two years. Mobay has its Bayblend® series of polycarbonate/ABS blends. These sacrifice some of polycarbonate's HDT and impact, while at the same time reducing the cost per cubic inch for applications not requiring all of polycarbonate's property profile. Applications include business machine housings. Xenoy resins are a family of resin blend products that have found extensive applications in such diverse arenas as automotive and medical applications.

Bumpers made of Xenoy resin are now featured on both European and United States automotive products (6). In this blend the chemical resistance of crystalline poly(butylene terephthalate) resin (PBT) is combined with the toughness of polycarbonate resin to yield the ductile, gasoline resistant, energy absorbing bumpers needed to meet national new car collision requirements.

In Table 3 a number of polycarbonate blending resins are listed that are now in commercial polycarbonate resin blends. It should be noted that not all blends need to be soluble blends. In these cases, sophisticated compatibilization technologies are incorporated.

The approach to market development for polycarbonate resins and their blends is changing. Formerly a one-to-one substitution of polycarbonate resin for glass or metal or other plastic was made with no change in design or molds. This often meant applying the resin to a part design which was simply a duplicate of a precursor glass or metal part, or an attempt to get the resin to produce the part in some existing plastic mold. This approach was reasonably effective but frequently led to over or under design. The copy approach also sacrifices some of the unique features of the new versatile plastic materials.

Suppliers are beginning to set up the staff and facilities necessary to support design system efforts. CAD-CAE (computer aided design-computer aided engineering) systems are now available to assist a customer in choosing the most economical resin and mold design in order to achieve his desired component performance. It is to be emphasized that the kind of designs produced are those characteristic of engineering resins. The designs do not necessarily have the form and shape one anticipates from classical metal, glass, wood, or ceramic materials.

Use of CAD-CAE is, of course, not unique to

Table 2. Typical Neat Polycarbonate Resin Applications.

Market	Application	Process Method		
		Injection Molding	Extrusion	Other
Transportation	Instrument panels	•		
	Public transport windows		•	
	Airplane canopies		•	•
	Lighting	•	•	•
	Fuses	•		
	Film		•	•
Housewares	Blenders	•		
	Power tool cases	•		
	Scraping implements	•		
Construction	Glazing		•	
	Lighting	•		•
	Signs			•
Sports Equipment	Goggles	•		
	Helmets	•		
	Surf boards			•
Medical	Containers	•		
	Tubing		•	
Electrical & Electronic	Housings	•		•
	Connectors	•		

Table 3. Polycarbonate Blending Resins.

Blending Resin	Soluble Blend?
Acrylonitrile-butadiene-styrene (ABS)	+
Styrenemaleic anhydride (SMA)	-
Poly(ethyleneterephthalate) (PET)	+
Poly(butyleneterephthalate) (PBT)	+
Poly(ester carbonate) (PEC)	+

polycarbonate resins. However, it is expected that computer-assisted design and development will make more effective use of polycarbonates. Further, in cases where current property profiles are inadequate for targeted applications, different polymers or blends may be specified. This will motivate further development of new resins and "tailored" blends.

CONCLUSION

Polycarbonate resins, and polycarbonate resins in many blends, continue to offer attractive combinations of engineering properties, processability, and design flexibility to the industrial community. Because of rapidly expanding activities in new resin and blend technologies and computer aided applications and design techniques, polycarbonate resin growth is being spurred outside the traditional material replacement markets. This growth may double polycarbonate resin use over the next several years. Because the markets are attractive, more companies will seek entry and competition will intensify internationally. Concurrently one can expect greater efforts at tailoring resins for specific customer applications and, hence, greater polycarbonate resin product differentiations between the various suppliers.

NOTE

Bayblend® is a registered trademark of Mobay Chemical Company.

Xenoy® is a registered trademark of General Electric Company.

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REFERENCES

1. H. Schnell, "Chemistry and Physics of Polycarbonates," Interscience (1964).
2. W. F. Christopher and D. W. Fox, "Polycarbonates," Reinhold (1962).
3. D. W. Fox, "Chemistry and Technology of Engineering Plastics," in "Applied Polymer Science," American Chemical Society, J. K. Cramer and R. W. Tess eds., pp. 433-435 (1975).
4. D. W. Fox and E. N. Peters, "Engineering Thermoplastics—Chemistry and Technology," in "Applied Polymer Science," 2nd ed., R. W. Tess and G. W. Poehlein, eds., American Chemical Society Symposium Series, Washington, in press.
5. H. Vernaleken, "Interfacial Synthesis," Vol. II, F. Millich and C. Carreher, Jr., eds., Marcel Dekker, Inc., New York, Ch. 3 (1977).
6. M. D. Bertolucci and D. E. DeLaney, 1983 National Technical Conference, Society of Plastics Engineers, Inc. September 20-22, 1983.

Properties of a Transparent Polycarbonate Copolyester Blend

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In recent years only a few totally new plastics have been developed, since suppliers are finding it quicker and less expensive to tailor existing resins to meet the requirements of a specific application by alloying. The properties of an alloy of polycarbonate and a proprietary copolyester have been fully characterized. Thermal analysis shows that the polymers are miscible in all proportions. Transparency, glass transition temperature, barrier properties, tensile, and flexural properties of the alloy all fall between those of the neat components. Certain synergistic properties were observed upon blending the polycarbonate and polyester. The tendency of the blend not to yellow during γ -sterilization is remarkably better than can be predicted by an additive relationship. Chemical resistance of the blends behaves in a similar manner. The excellent balance of properties exhibited by the blend such as transparency, impact strength, γ -radiation resistance, and chemical resistance makes it useful in applications such as medical disposables and filter bowls.

INTRODUCTION

For many years the plastics industry has tailored the properties of their resins to suit the requirements of specific applications by polymer blending. The advantages of this approach over developing a totally new polymer or copolymer is that polymer blending is quicker—averaging only two years from conception to commercialization for a blend versus about ten years for a new polymer. Additional benefits of polymer blending include low capital investment and extension of plant capacity. This paper describes how several key properties of polycarbonate resin can be improved by blending it with a miscible copolyester.

EXPERIMENTAL

Materials

The polycarbonate used is General Electric Company's Lexan® 100 resin supplied without added thermal stabilizers or tints. It has an intrinsic viscosity in CHCl_3 of 0.55 dl/g at 25°C.

The copolyester used is based on 1,4 cyclohexanedimethanol and a 20/80 mixture of isophthalic and terephthalic acids. It has an intrinsic viscosity of 0.78 dl/g in 60/40 w/w phenol/1,1,2 trichloroethane (TCE) at 25°C.

Polycarbonate/copolyester blends are commercially available from General Electric Company as Xenoy™ 3000 series resins.

Processing

Polymer blends were prepared by mixing polycarbonate and copolyester along with <1 weight percent of a color stabilizer. This mixture was then melt mixed on a 1-inch, 25 L/D single screw extruder, and the extrudate pelletized. Pelletized material was dried 4 h at 110°C prior to molding ASTM specimens on a 5 oz. capacity injection molding machine. A stock temperature of 280°C was employed with a mold temperature of 70°C.

Irradiated Samples

Gamma irradiations were carried out in air utilizing a cobalt-60 source. Several commercial irradiation facilities were used. Sample positioning was on carrier unless otherwise specified with a dose rate of ~0.13 Mrad/h.

Testing

Yellowness Index was determined on a Pacific Scientific Spectrogard II unit according to ASTM D1925 using 0.125-inch injection molded plaques. Readings were taken as soon as received from irradiation.

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Chemical resistance was determined on 1 percent constant strain jigs using 0.5- by 0.125- by 2.5-inch unannealed injection molded bars. Dioctyl phthalate (DOP), medical grade (Hateco Chemicals Co.) was wiped on prior to placing in a 60°C (140°F) air circulating oven.

MORPHOLOGY

As has been thoroughly discussed in detail by other authors (1 to 3) generally two types of morphologies are possible on a molecular level for polymer blends. In an attempt to simplify the thermodynamic arguments for these morphologies, a schematic representation of each is shown in Fig. 1a and 1b. Figure 1a shows an idealized morphology of an immiscible two phase blend. Polymer A molecules reside primarily in discontinuous domains surrounded by a continuous phase of polymer B molecules. Figure 1b shows the alternative—a one phase miscible blend. Here the polymer molecules have sufficient attractive forces to allow mixing on a molecular level. For commercialization, a one phase miscible blend is almost always preferred over a two phase blend because the former processes more like a copolymer than a blend (two phase). A two phase system can have shear induced lamination of the phases during the processing, which can cause properties to vary with orientation or cause delamination of the phases when processed parts are stressed. Unfortunately, it is relatively rare that two polymers picked at random will be miscible since specific attractive polymer-polymer interactions are necessary for miscibility (4).

Figure 2 shows a differential scanning calorimetry (DSC) scan of the neat polymers and a 50/50 blend of polycarbonate and copolyester. The single glass transition temperature of the blend is evidence for miscibility. Figure 3 shows that a single glass transition temperature is observed throughout the entire composition range and that its value is additive with composition. As expected, the heat deflection temperature parallels the glass transition temperature but is roughly 20°C lower in value. Further evidence for polymer-polymer miscibility is shown in Fig. 4, where the polycarbonate/copolyester blend maintains a high degree of transparency throughout the composition range. This usually indicates there are no discontinuous phases to refract light.

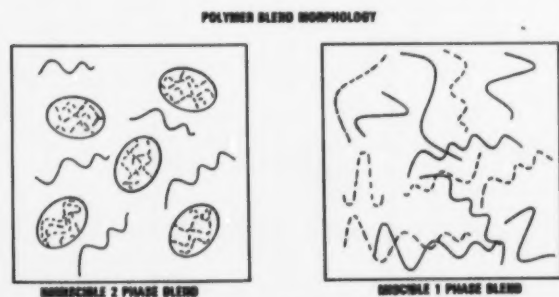


Fig. 1. Schematic representation of immiscible and miscible blends.

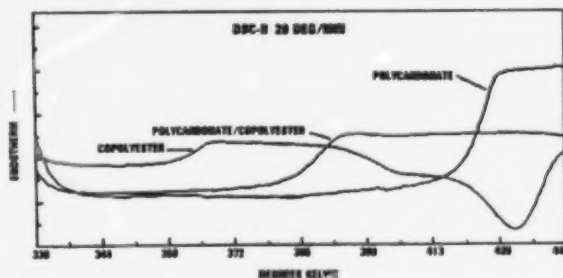


Fig. 2. Differential scanning calorimetry scan of the neat copolyester, polycarbonate, and a 50/50 blend showing the glass transition temperature endotherms.

THERMAL PROPERTIES

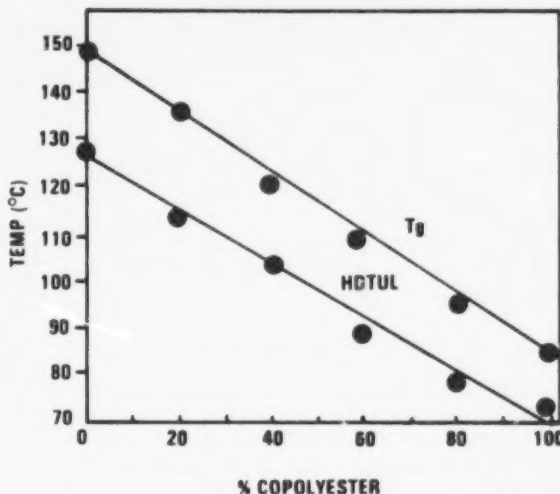


Fig. 3. Glass transition temperature (T_g) and heat deflection temperature under load (HDTUL) as function of blend composition.

OPTICAL PROPERTIES

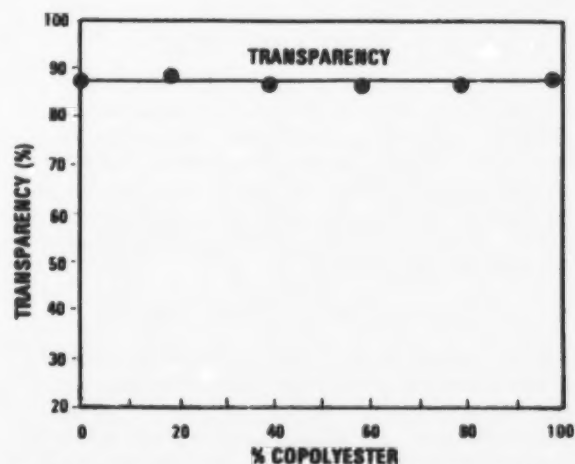


Fig. 4. Percent transparency as a function of blend composition.

MECHANICAL PROPERTIES

Figure 5 is a plot of the tensile and flexural properties as a function of blend composition. In all

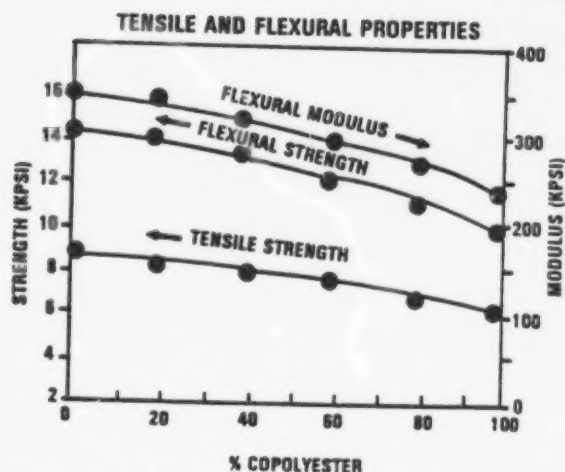


Fig. 5. Tensile and flexural properties as a function of blend composition.

cases the property for the blend lies between that of the neat polymers, but there is a slight positive deviation from linearity. This phenomenon is usually attributed to densification due to better molecular packing caused by the attraction between polymer molecules (5).

CHEMICAL RESISTANCE

Generally amorphous polymers are susceptible to stress cracking when contacted by solvents and polycarbonate is no exception. Table 1 shows that adding copolyester to the polycarbonate dramatically improves the stress-crack resistance to dioctyl phthalate (DOP). This is valuable property since few transparent amorphous plastics can be used in contact with plasticized PVC because of stress cracking. Similar improvements in chemical resistance for the blends have been observed with many other chemicals.

BARRIER PROPERTIES

Adding the miscible copolyester to the polycarbonate also lowers the gas transmission rate, thereby improving the barrier properties of the material. In particular the transmission rate for CO₂ as a function of added copolyester is demonstrated in Fig. 6. The transmission rates for H₂O and O₂ follow a similar pattern, decreasing in value with additional copolyester.

γ-RADIATION RESISTANCE

The γ-radiation method for sterilizing disposable medical parts is predicted to double in ten years (6) due to concern over health and fire issues associated with ethylene oxide sterilization. Unfortunately, many transparent plastics used to fabricate medical disposables either yellow or lose properties upon γ-irradiation. Figure 7 shows that the tendency of polycarbonate to yellow during γ-irradiation is markedly reduced by the addition of low levels of copolyester. The reduced yellowing is far superior to what can be predicted by simple dilution effects.

Table 1. Effect of Elevated Temperature—Dioctyl Phthalate Exposure on Polycarbonate/Copolyester Blends.

Blend Composition			Effects
% Polycarbonate	% Copolyester	% Strain	
100	0	1.0	Very severely cracked after <15 min.
90	10	1.0	Severely cracked after <1 h completely broke off jig after 18 h.
80	20	1.0	Severely cracked after ~1 h, raising off jig after 18 h.
70	30	1.0	Slightly crazed after ~1 h, crazed after 18 h.
60	40	1.0	Very slightly crazed after 1 h, slightly crazed after 18 h.
50	50	1.0	Very slightly crazed, with no cracking after >60 days.

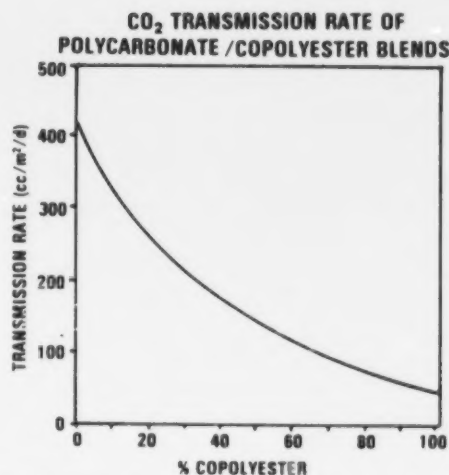


Fig. 6. Transmission rate of carbon dioxide (CO₂) as a function of blend composition.

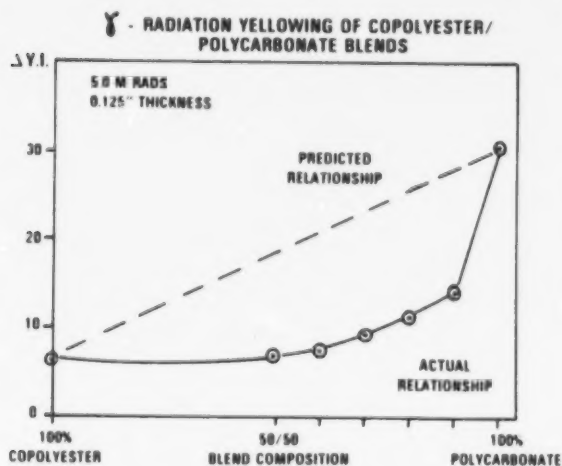


Fig. 7. Effect of blend composition on yellowing after gamma-irradiation.

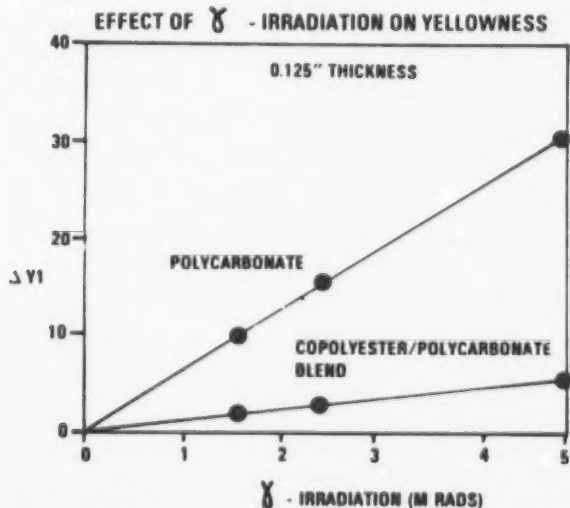


Fig. 8. Effect of gamma radiation dose on yellowing of a 50/50 polycarbonate/copolyester composition.

Table 2. Effect of Gamma Irradiation on a Polycarbonate/Copolyester Blend.

	Non-irradiated	1.5 Mrad	2.5 Mrad	5.0 Mrad
Impact strength (% samples ductile @ 320 in-lb impact)	100	100	100	100
Intrinsic viscosity in phenol/TCE	0.65	0.66	0.66	0.66
Chemical resistance to 60°C DOP	No cracking	No cracking	No cracking	No cracking
Tg (°C)	114	114	114	114
		Same as non-irradiated	Same as non-irradiated	Same as non-irradiated

This suggests to us that the polyester may be interfering with polycarbonate free radical species formed during irradiation. Figure 8 shows the effect of radiation dose on yellowness for a 50/50 polycarbonate/copolyester blend. The rate of yellowing for the blend is roughly five times less for the blend than for neat polycarbonate.

In addition to color retention during γ -radiation, the polycarbonate/copolyester blend also maintains its physical properties up to at least 5 Megarads dose. Table 2 shows that key physical properties are maintained.

CONCLUSIONS

Several properties of polycarbonate can be improved without sacrificing transparency, mechanical properties, or processability by blending it with miscible copolyester. These include:

- Improved chemical resistance,
- Improved γ -radiation resistance, and
- Improved barrier properties.

ACKNOWLEDGMENTS

We would like to thank Drs. Kurt Feichtinger and Ron LaRochelle for their helpful discussions and to our technicians Jim Jones and Dave Leibinger for their efforts in this program. A special thanks is given to Mr. Tom Sauer for his help.

REFERENCES

1. S. Krause, "Reviews in Macromolecular Chemistry," Vol. 8, p. 251, Butler, O'Driscoll and Shen, eds., Marcel Dekker, Inc., New York (1972).
2. A. R. Schultz, *Am. Chem. Soc., Div. Polym. Chem. Polym. Prepr.*, 8, 1455 (1967).
3. D. R. Paul, "Polymer Blends," Vol. 1, p. 7, D. R. Paul and S. Newman, eds., Academic Press, New York (1978).
4. O. Olabisi, L. M. Robeson, and M. T. Show, "Polymer-Polymer Miscibility," p. 26, Academic Press, New York (1979).
5. A. F. Yee and M. A. Maxwell, *J. Macromol. Sci.-Phys.*, B17, 557 (1980).
6. R. S. Melberg, "Radiation Processing," Research Report 618, SRI International, Menlo Park, Calif. (1979).

The Unique Properties of Silicone and Fluorosilicone Elastomers

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In this paper a brief description of the synthesis of silicone polymers and their compounding is given, and the wide range of properties available in Silastic[®] silicone rubber is discussed. Some of the key properties are related to several applications. These include mechanical properties, chemical and environmental resistance, thermal stability, electrical properties, flame resistance, and surface characteristics. Silicone rubber parts are currently used in the automotive, electronic, dairy, medical, construction, and aerospace industries. Among the applications discussed are axle seals, hose, milk inflations, wire and cable insulation, and elastomeric keyboard springs. In addition, improved silicone rubber materials are being developed for new applications.

INTRODUCTION

Because of their unique properties, silicone rubbers are being used in an increasing number of applications. One type of silicone rubber which has these properties is the Silastic brand of silicone rubbers. This paper describes the versatility of these elastomers by relating key properties to several applications.

The silicon-oxygen linkage ($-\text{Si}-\text{O}-\text{Si}-\text{O}-$) that makes up the backbone of silicone polymers is the same bond found in other high-temperature materials such as sand and glass. This bond is the primary reason for silicone rubber's high temperature resistance. The flexibility and high free volume of this chain contribute to the excellent low temperature properties and high gas permeability. By replacing one methyl group on each silicon atom with a trifluoropropyl group ($-\text{CH}_2-\text{CH}_2-\text{CF}_3$), the final result is a fluorosilicone polymer that has superior fuel resistance along with higher specific gravity and lower gas permeability than dimethyl silicone elastomers. Other properties are similar.

Although silicone rubbers are indeed well-known for their broad service temperature range (-100 to $+316^\circ\text{C}$), other unique features are leading to expanded uses.

Silastic silicone rubbers function with reliability in adverse environments due to their resistance to ozone, corona, moisture, radiation, and weathering. In addition, they show favorable flame characteristics, bacteria resistance, physiological inertness, excellent electrical properties, good release or anti-stick characteristics, high chemical resistance, good

processing properties, and good fatigue and cut growth resistance.

Among the new applications and areas of increased use for silicone rubber are: drive axle seals and ignition system components in automobiles and trucks; exterior and interior seals for aircraft; tubing, gaskets, and milking machine inflations in the dairy industry; glazing gaskets for construction; and respirator parts, bottle stoppers, and tubing in the health care industry.

The objective of this paper is to discuss the chemistry and characteristics of these rubbers, as well as their relationship to existing and emerging applications.

THE CHEMISTRY OF SILASTIC SILICONE RUBBER

Polymers

One of the basic polymers used to compound Silastic silicone rubber is poly(dimethylsiloxane). The manufacture of this polymer begins by reacting silicon dioxide with coke in the presence of heat to produce silicon metal. This elemental silicon is reacted with methyl chloride in the presence of a catalyst and heat to produce chlorosilanes. Through a distillation procedure, dimethyldichlorosilane is separated and then hydrolyzed to form dimethylsilanediol. This diol is condensed to form cyclic siloxanes, mostly the tetramer. The tetramer is then polymerized in the presence of a catalyst and heat to form polydimethylsiloxane. Figure 1 summarizes the series of reactions in this process.

In addition to dimethylsiloxane polymers, three organic groups are commonly substituted on the silicon atom to replace methyl groups (see Fig. 2).

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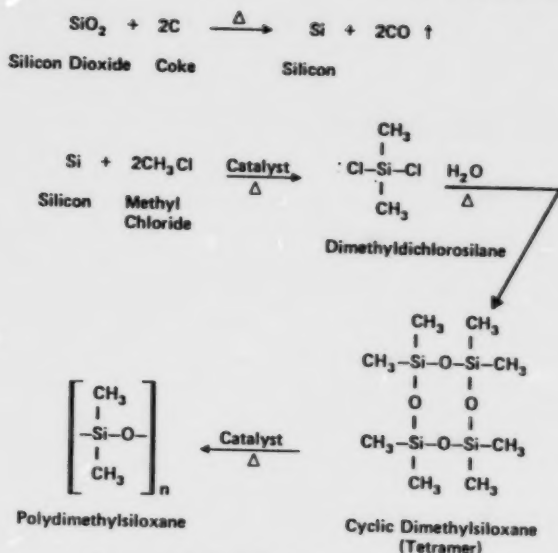


Fig. 1. Polydimethylsiloxane synthesis.

R Group Is		Polymer Classification (ASTM D-1418)
$\begin{array}{c} \text{H} \\ \\ \text{Methyl} - \text{C} - \text{H} \\ \\ \text{(CH}_3\text{)} \end{array}$	Basic Silicone Properties	MQ
$\begin{array}{c} \text{Phenyl} \\ \text{(C}_6\text{H}_5\text{)} \end{array}$	Increase Low Temp. Flex - 180°F	PMQ or PVMQ
$\begin{array}{c} \text{H} \\ \\ \text{Vinyl} - \text{C} = \text{C} - \text{H} \\ \quad \\ \text{(CH}_2=\text{CH)} \quad \text{H} \end{array}$	Faster Vulcanization, Higher Cross-Link Density	VMO
$\text{Trifluoropropyl (CH}_2\text{CH}_2\text{CF}_3\text{)}$	Fuel And Solvent Resistance	FVMO

Fig. 2. Silicone polymers.

These groups are vinyl, phenyl, and trifluoropropyl.

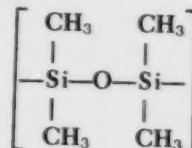
Vinyl groups are added to improve vulcanization rate and compression set. In general, about 0.1 to 0.6 mole percent methylvinylsiloxane units are copolymerized into the polymer chain.

Phenyl groups are added to improve low-temperature performance, to enhance radiation resistance, and to lower resilience. The substitution of phenyl for methyl lowers the brittle point to -116°C (-178°F) from -73°C (-100°F). The large, bulky phenyl groups break up the regularity of the polymer, causing a disruption in crystallinity, which results in better low-temperature properties. The commonly used polymers in this process are either copolymers of phenylmethylsiloxane-dimethylsiloxane or diphenylsiloxane-dimethylsiloxane.

Trifluoropropyl groups ($-\text{CH}_2-\text{CH}_2-\text{CF}_3$) as previously discussed are added to increase resistance to fuels, oils, and solvents. The high polarity of this polymer results in superior resistance to attack by nonpolar (most hydrocarbons) and slightly polar solvents compared to the performance of the nonpolar methyl group polymer. As one might expect, this elastomer is more susceptible to attack by polar solvents (such as esters and ketones) than is the polydimethylsiloxane elastomer.

Reinforcement

Silicone polymers are generally reinforced with fumed and/or precipitated silica fillers. The silica filler is basically silicon dioxide (SiO_2) with a number of hydroxyl groups on the surface of the filler aggregate. The primary sites within the silicone polymer that interact with the silica are terminal silanol groups and oxygen atoms in the polydimethylsiloxane segments



of the polymer chain. Figure 3 shows possible interactions between the polymer chain and the silica filler. The nature of the interaction is believed to be primarily the result of hydrogen bonding and van der Waals forces rather than chemical bonding.

This phenomenon leads to high levels of bound polymer and increased tensile strength. Typical tensile strengths of crosslinked polymers can be increased from 50 psi (0.34 MPa) for the nonreinforced polymer to 1500 psi (10.3 MPa) for the reinforced polymer.

However, these interactions can also result in a phenomenon known as crepe hardening, producing rubbers that require long mill softening times. Low viscosity silicone fluids with hydroxyl-group functionality are added to reduce crepe hardening. These fluids are adsorbed on the surface of the silica, reducing its interaction with the polymer.

Compounding

Like other rubbers, Silastic silicone rubbers can be compounded to meet a variety of economic and

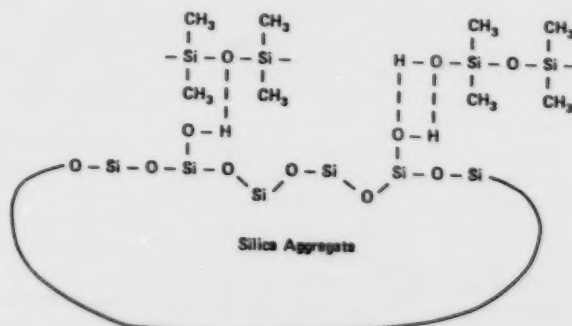


Fig. 3. Silicone polymer-silica interactions.

physical requirements. Compounding ingredients may be added to increase temperature performance, flame retardance, or resistance to greases, oils, or fuels. There are several types of common compounding ingredients.

Extending fillers may be added to lower cost, increase hardness and modulus, and to lower oil swell. Commonly used extending fillers are ground quartz and diatomaceous earth; calcium carbonate and clays are also used.

Commercially available modifiers are used to increase flame resistance, enhance high-temperature performance, improve extrudability, enhance mold release, and increase oil resistance. Pigments may be added to impart color. Table 1 lists typical formulation components of commercial silicone rubber.

Curing

Some Silastic silicone elastomers are peroxide-vulcanized by a free radical mechanism involving the unsaturated vinyl pendant groups that have been incorporated into the basic polymer structure. Peroxide-initiated crosslinking results in carbon-carbon bonds created by the reaction of free radicals. The free radicals are generated in the polymer via the peroxide radicals either by abstracting hydrogen from methyl or by adding to a vinyl group.

Other cure mechanisms are via radiation (Cobalt 60) or by addition of polyfunctional silicone hydrides to unsaturated groups along the poly(dimethylsiloxane) chain by use of a metal catalyst. The three types of cures described are classified as activated, because all require the application of energy, either in the form of heat or radiation.

PROPERTIES OF SILASTIC SILICONE RUBBER

Silastic silicone rubbers can be compounded to meet a variety of specialized requirements; resulting physical properties of vulcanized material depend upon the compounding formula and the fabrication method. The data shown in Table 2 represent typical ranges of properties of these poly(dimethylsiloxane) silicone rubbers.

These rubbers are permeable to many gases, including oxygen and water vapor. They are extremely resistant to weathering, oxidation, ozone, water, and corona. In addition, they can be formulated to resist radiation, coolants, fuels (as in the case of fluorosilicone), oils, greases, and weak acids and bases. Silicone elastomers can also be compounded to meet FDA regulations for food contact (21 CFR 177.2600).

Table 1. Typical Formulation Components of Commercial Silicone Rubber.

Materials	Parts By Weight
Base	100
Filler	1-150
Modifiers	0.1-20
Pigments	0.1-2
Peroxides	0.4-3

Silastic silicone rubber is serviceable from -100 to +316°C (-418 to 600°F), a range that is unmatched by organic elastomers. One of the most outstanding characteristics of silicone elastomers is their ability to retain a high percentage of their room temperature properties when operating at elevated temperatures (Fig. 4). Organic elastomers under similar conditions show less retention of elongation than silicone elastomers. Properties at temperature are important because parts can be expected to fail under operating conditions rather than under nonoperational, ambient conditions.

These materials have inherently good insulating properties. In addition, these properties remain fairly constant when exposed to adverse environments. Table 3 shows typical electrical data. Also, these silicone rubbers can be compounded to be electrically conductive, having a conductivity of 0.2 siemens (a resistivity of 5 ohm-cm). Additionally, they can be compounded to show a good balance of flame characteristics to meet a variety of specifications, including UL 94 V-0 and V-1, BMS 1-59C, BMS 1-63A, and UL Code 62.

Because Silastic silicone rubbers contain low

Table 2. Typical Property Ranges of Dimethyl Silicone Rubber.

Plasticity, Inches (mm)	0.075-0.180 (1.91-4.57)
Specific Gravity	1.07-1.70
Hardness, Shore A-2	25-80
Tensile Strength, psi (MPa)	800-1500 At 22°C (5.5-10.3) 350-650 At 204°C (2.4-4.5)
Elongation, Percent	100-900 At 22°C 60-480 At 204°C
Modulus At 100%, psi (MPa)	50-900 (0.3-6.2)
Compression Set, Percent (22 Hrs./177°C)	10-40
Tear, Die B, ppi (kN/m)	60-300 At 22°C (10.5-52.5)
Resilience, Percent	30-60
Cut Growth—DeMattia Flex Cycles To Grow 0.5 Inch	75-1,500,000

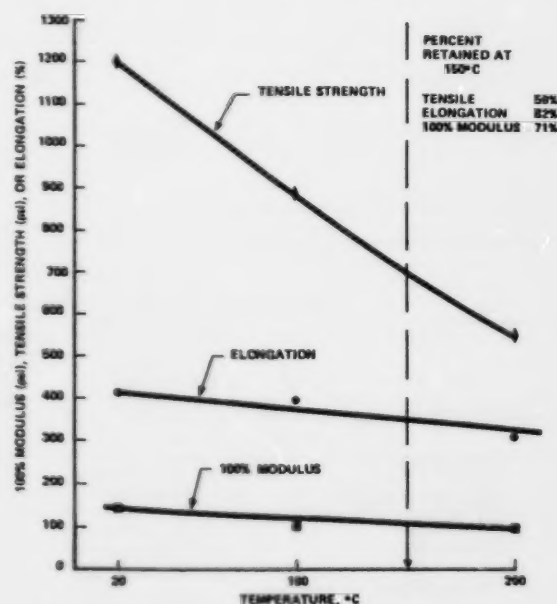


Fig. 4. Retention of properties versus temperature.

levels of carbon and no halogens, they show low smoke density and toxicity when compared with other commonly used compounds (Table 4). The exception is fluorosilicone rubber, which like other fluoropolymers evolves toxic gases when burned.

These silicone rubbers have several unique surface properties. These include low surface tension and coefficient of friction values ranging from 0.25 to 0.75. These elastomers also resist attack by fungi and other microorganisms. Recent studies have shown that some such silicone rubber parts resist surface cracking more than similar parts made from certain organic elastomers.

PROPERTIES OF SILASTIC FLUOROSILICONE RUBBER

The properties of fluorosilicone elastomers depend on the product used and the recipe chosen. The data shown in Table 5 represent the typical range of properties of Silastic fluorosilicone rubbers.

Performance at Temperature

Fluorosilicone elastomers retain a high percentage of their room temperature properties at temperature. In this respect, they are very similar to the poly(dimethylsiloxane) elastomer shown in Fig. 4. Most other organic elastomers under similar conditions show less retention of elongation properties than fluorosilicone elastomers. Measuring properties at temperature is important because parts can be expected to fail under actual operating conditions.

Low Temperature Properties

The low temperature properties of Silastic fluorosilicone elastomers are outstanding. The chain

flexibility of this polymer is clearly demonstrated by measurement of the TR-10 (100 percent elongated samples were frozen and warmed until they had retracted to 10 percent of their original extension) value of -60°C (-75°F). The brittle point is -68°C (-90°F), which suggests that static applications with fluorosilicone elastomers are possible at temperatures below TR-10.

Fuel Performance

Fluorosilicones are the only fuel-resistant elastomers which will remain serviceable from -68 to 232°C (90 to 450°F). As already stated, the primary reason for employing fluorosilicone rubber is that of excellent fuel resistance. A 70 durometer Silastic fluorosilicone rubber was selected for evaluation. Figure 5 shows the effect of selected fuel media on the hardness change versus immersion time. JP-8 has the least effect; the no-lead gasoline/methanol mixture is the most severe. The shorter lines for JP-8 and other fuels in subsequent graphs do not constitute failure; rather, they represent an immersion time of one week. An important property characteristic to note is the leveling or stabilizing effect that occurs after the first twenty-four hours. With longer immersion times very little change occurs; the major change takes place within the first day.

The effect of these various fuels on tensile strength and elongation are shown in Figs 6 and 7. Gasohol in this study is represented by a 10 volume percent ethanol and 90 percent unleaded gasoline mixture. After the first twenty-four hours, the retention of both properties stabilize as immersion time increases. This performance allows the fabricator and end user to predict how these fluorosili-

Table 3. Electrical Properties of Silicone Rubber.

Dielectric Strength		Dissipation Factor	
Volts/Mil (.065 Inch Slab)	500	10^2 Hz	0.002
		10^6 Hz	0.0027
Dielectric Constant		Volume Resistivity	
10^2 Hz	3.02	OHM-cm	2.0×10^{15}
10^2 Hz	3.01		
Insulation Resistance megohms/1000 ft.		20,000	

* 0.030 inch Wall Insulation Extruded Over Number 18 AWG Stranded Wire.

Table 5. Typical Property Ranges.

Specific gravity	1.35-1.65
Hardness, Shore A-2	35-80
Tensile strength, psi (MPa)	800-1400 @ 22°C (5.5-9.6)
	350-600 @ 204°C (2.4-4.1)
Elongation, percent	150-500 @ 22°C
	90-300 @ 204°C
Modulus @ 100%, psi (MPa)	80-900 @ 22°C (0.55-6.2)
Compression set, % (22 hrs/ 177°C)	12-35
Tear, die B, ppi (kN/m)	60-265 @ 22°C (10.5-46.4)
Temperature range	-68°C to 232°C

Table 4. Smoke Evolution Data by National Bureau of Standards Smoke Chamber Test.

Material	Exposure (F-Flaming) (N-Nonflaming)	Maximum Opti- cal Density (Dm)	Time To Reach Dm Of 16 (Min- utes)	Max Gas Conc in PPM		
				CO	HCl	Others
PVC, Plasticized	F	199	0.4	420	450	—
Fluoropolymer	N	180	1.4	500	450	—
	F	109	1.2	480	—	HF, 80
Chlorosulfonated	N	75	2.5	20	—	HF, 90
	F	230	0.8	750	400	SO ₂ , 50
Polyethylene	N	196	1.1	60	200	SO ₂ , 40
Chloroprene	F	233	0.7	550	200	—
Silicone Rubber	N	161	1.6	100	200	—
	F	151	0.9	60	—	—
	N	44	2.8	10	—	—

Loss in Durometer Points in Different Media vs Immersion Time

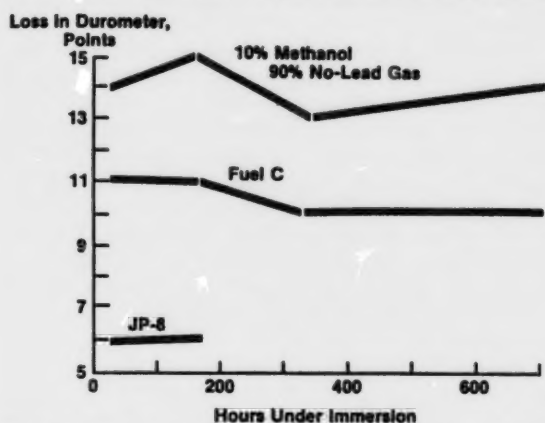


Fig. 5. Loss in durometer points in different media versus immersion time.

Percent Retention of Tensile in Different Media vs Immersion Time

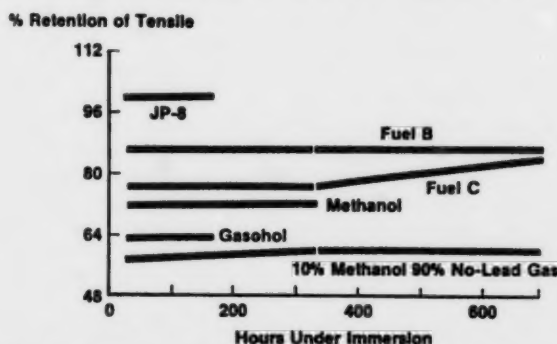


Fig. 6. Percent retention of tensile in different media versus immersion time.

Percent Retention of Elongation in Different Media vs Immersion Time

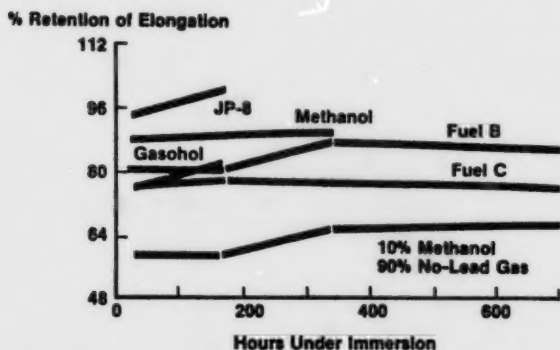


Fig. 7. Percent retention of elongation in different media versus immersion time.

cone elastomers will function during long periods of immersion.

Volume swell in fuels follows the same pattern as

shown in previous graphs. The initial swell of the 70 durometer Silastic fluorosilicone rubber occurs during the first twenty-four hours; after this time there is very little change (Fig. 8). The effect of Fuel C on volume swell at room temperature and 100°C is shown in Table 6.

Many of the fuel-resistant elastomers on the market today, if subjected to these conditions, show a two-fold increase or more in volume swell in Fuel C at 100°C. This test shows that the effect of immersion at high temperatures on this fluorosilicone elastomer is minimal.

Sour gasoline is another medium which attacks certain fuel-resistant elastomers. Sour gasoline is formed when fuel reacts with oxygen to form hydroperoxides. The hydroperoxides decompose into free radicals, which chemically attack the surface of the elastomer and cause embrittlement or reversion to occur. Silastic fluorosilicone elastomers withstand this type of chemical attack. The rubber remains completely flexible and has good retention of properties; see Table 7.

Special attention has been given to fluorosilicone elastomers in different fuels and at various temperatures. These data that have been presented demonstrate the viability of fluorosilicone elastomers for various fuel applications as the environment dictates.

Percent Volume Swell in Different Media vs Immersion Time

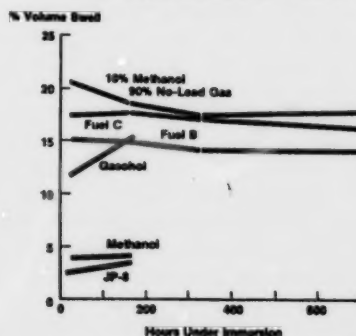


Fig. 8. Percent volume swell in different media versus immersion time.

Table 6. Percent Volume Swell in Fuel C*.

70 durometer fluorosilicone rubber	
Room temp./70 hours	17.7
100°C/70 hours	20.9

* ASTM D471-77. Reference Fuel C, a 50:50 volume percent mixture of isooctane and toluene.

Table 7. A Fluorosilicone Elastomer's Performance in Sour Gasoline.

Aged 17 days @ RT in sour gasoline*	70 durometer fluorosilicone rubber
Durometer change, pts.	-12
Tensile change, %	-26
Elongation change, %	-17
Volume change, %	+13.5

* Indolene HO-II/1-butyl hydroperoxide mixture—50/1.

APPLICATIONS OF SILASTIC SILICONE/ FLUROSILICONE RUBBERS

Because of the array of properties that can be achieved by varying formulation and fabrication processes, Silastic silicone rubbers have a wide range of applications. Parts made from these rubbers have become important in the automotive, electrical, defense, and construction industries. Some of these elastomers have fulfilled specialized needs in the appliance, dairy, and food processing industries; and they have contributed to the advancement of technology in the aerospace, electronics, and medical fields.

One of the new, front-wheel drive, U.S.-made automobiles uses a tear-resistant Silastic silicone rubber boot to protect one of its four inboard axle joints. This boot is made from a material featuring a tensile strength of 1250 psi (8.6 MPa) and a tear strength of 220 ppi (38.5 kN/m). This compound also meets flex and grease resistance requirements at both high and low temperatures.

Silastic fluorosilicone elastomers are currently used to make exhaust gas recirculating (EGR) diaphragms for some passenger cars. An EGR diaphragm recirculates the exhaust gases through a valve and back into the air/fuel stream of the carburetor. Silastic fluorosilicone rubber has the necessary resistance to gasoline and its vapors, along with the needed high and low temperature performance for these conditions.

A successful use of Silastic fluorosilicone rubber has been as O-rings on the fuel line manifold for the McDonnell Douglas DC-8 (and DC-9) aircraft. These lines have many couplings that allow flexing and movement as the wing bends during flight. It also allows for expansion and contraction during temperature changes. There are 420 couplings per airplane (DC-8) using 840 O-rings. During testing, McDonnell Douglas subjected these fluorosilicone rubber seals to a total of over 9 million flex cycles and nearly 3 million pressure cycles in jet fuel without leakage or failure.

Silastic silicone rubber has been used for the past several years to fabricate spark plug boots and to insulate ignition wire. Conductive Silastic silicone rubber is used as a conductor replacing the metal core. The major U.S. automotive companies have

made silicone rubber the standard material in these applications, and the aftermarket will continue to expand for silicone rubber boots and insulated ignition wire.

With the advent of emission controls, higher temperatures, and high-energy ignition (30–40 kV), such silicone rubbers are the logical choice for ignition system components. Their electrical properties and resistance to heat have extended the life of these parts to 50,000 miles or more. These elastomers are used in a variety of demanding hose applications, including heater and coolant hose for trucks, buses and heavy equipment, as well as turbocharger hose. The excellent resistance to heat and coolant exposure leads to a hose life of approximately 500,000 miles.

Some Silastic silicone rubbers have sufficient green strength to allow processing on equipment designed for producing organic hose. This has lowered the production costs of making silicone hose.

Silastic silicone rubber gaskets are used to seal windows and doors on modern commercial aircraft. Excellent weatherability and low-temperature performance make this silicone rubber effective for these types of exterior seals. Flame characteristics and the ability to be pigmented to any color have made it suitable for interior seals as well. Some Silastic silicone rubbers are available to meet aircraft specifications such as BMS 1-57D, BMS 1-59C, BMS 1-63A, DMS-2012, and DMS-1506.

Silastic silicone rubber is used as insulation for many types of wire and cable, including appliance wire, motor lead wire, instrumentation and critical control cable, and these elastomers are available to meet many wire and cable specifications, including UL62 Class 22, UL44 Type SA, Mil-W-8777C, and Mil-C-915.

The excellent service life of Silastic silicone rubber at high temperatures, along with its insulative properties and flame resistance, make it desirable for electrical applications. Table 8 summarizes the behavior of Silastic silicone rubber at high temperatures.

Silastic silicone rubber has found a new application in the rapidly advancing electronics industry. Elastomeric keyboard springs are being designed for calculators, telephones, and data entry terminals. Even after millions of key depressions, a Silas-

Table 8. UL Heat—Aging Tests of Silastic® WC-50 Silicone Rubber.

As Vulcanized	UL-62 Class 22 Requirements	UL Style 3257 Requirements	Actual Properties
Tensile Strength, psi (MPa)	500 (3.44)	900 (6.20)	1271 (8.76)
Elongation, Percent	100 Min.	250 Min.	450
Oven Aged 60 Days At 210 °C			
Tensile Strength, psi (MPa)	500 (3.44)	—	1041 (7.17)
Percent Retained	60	—	81
Elongation	—	—	320
Percent Actual	50	—	76
Percent Retained	25	—	—
		30 Days At 260 °C	60 Days At 250 °C*
Tensile Strength, psi (MPa)		450 (3.10)	509 (3.51)
Elongation, Percent		50	150

* Values Obtained At Conditions Different From Those Of Specification.

tic silicone rubber used in these springs features excellent flex life and constant modulus. Conductive Silastic silicone rubber buttons are used to complete the circuit.

In the medical field, high-strength Silastic silicone rubbers are used to produce tubing and bellows for use on hospital respirators. They permit both hot and cold sterilization of these units. The excellent flexural strength of some of these elastomers, plus their physiological inertness, make them useful for respirator parts.

Silastic silicone rubbers are finding a new use in the dairy barn. Recent work by Noorlander and Heckmann at Brigham Young University has shown that Silastic silicone rubber is an excellent material for use in milk contact applications. Using scanning electron microscopy (SEM), elemental X-ray analysis (EPAX), and microbiological methods, the researchers have shown that inflations made from organic elastomers show surface cracks that widen with use. These cracks harbor bacteria that cause mastitis. In contrast, Silastic silicone rubber exhibits a smooth surface and resists cracking for thousands of milkings, and will therefore not provide a haven for mastitis-causing bacteria.

Applications for Silastic silicone rubber continue

to increase over a broad range of fields and industries. In addition to the examples discussed here, these elastomers may be found in copier rolls, laminator press pads, flexible heaters, shaft seals and O-rings, connectors, flame-resistant hose covers, glazing gaskets, bottle stoppers, and drip irrigation emitters.

SUMMARY

A review of the useful properties of Silastic silicone rubber and a few of its uses have been discussed. In addition to its temperature performance, Silastic silicone rubber exhibits many useful characteristics. These include a wide range of physical properties, electrical insulation or conductivity features, excellent flame characteristics, and unique surface qualities.

Silastic fluorosilicone elastomers likewise exhibit a combination of useful properties. Fuel data indicate that the long-term performance of these elastomers is predictable after the initial twenty-four hours of immersion testing. Of the fuel-resistant elastomers on the market today fluorosilicone rubber has one of the widest temperature operating ranges (-68 to 232°C).

Victrex® Poly(ethersulfone) (PES) and Victrex® Poly(etheretherketone) (PEEK)

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Properties of two high performance engineering thermoplastics, amorphous polyethersulfone (PES) and semicrystalline polyetheretherketone (PEEK), are discussed. Both resins can be processed by conventional techniques, compounded with high performance fibers, and have high service temperature (up to 300°C). Due to the amorphous character PES can be dissolved and spray coated into metals.

INTRODUCTION

VICTREX® poly(ethersulfone) (PES) has been established in the marketplace for a number of years. It is a typical engineering thermoplastic at room temperature: tough, strong, and rigid but distinguished by excellent high temperature performance, low flammability, and smoke emission. Poly(ethersulfone)'s uses cover a range of industries and include such applications as coil formers, connectors, terminal blocks, hot water meters, reflectors, medical components, bearings, metal coatings, and the matrix for high performance composites.

A more complete description of PES would be an amorphous, engineering thermoplastic; it possesses all the strengths and weaknesses of amorphous thermoplastics. Poly(etheretherketone) (PEEK), on the other hand, is a high temperature, crystalline thermoplastic and as such provides a natural complement to PES (See Fig. 1 for structures). In certain areas, temperature service range (300°C), mechanical strength, and chemical resistance of PEEK's performance exceeds the performance of PES. Between them, PES and PEEK offer an unrivalled selection of properties to the design engineer (1 to 3).

PROCESSING

PES and PEEK are true thermoplastics. They can be compression molded, injection molded, and extruded using conventional equipment. Regrind can be reused, as with other thermoplastics, and processing times are comparable with those of conventional engineering thermoplastics. Both PES and PEEK require drying prior to use and their processing temperatures are high, with barrel temperatures in the range 340 to 400°C and mold temperatures 140 to 180°C. These temperatures are, however, within the heating capabilities of conventional processing equipment.

Mixtures of PEEK or PES with continuous carbon or other high performance fibers provide high

strength, high temperature composites which can be shaped by thermoforming.

The crystalline nature of PEEK admits it to orientation processes to provide high strength, high temperature monofilament, while its chemical resistance and low flammability make it a suitable candidate for wire coating using melt extrusion. The solubility of PES in certain polar solvents can be turned to advantage in that it can be sprayed onto metal either by itself or in conjunction with PTFE to provide decorative or nonstick coatings. By virtue of its solvent resistance, PEEK is precluded from such spraying techniques. PEEK coatings can be applied to metal; powder coating technology is the route.

MECHANICAL PROPERTIES

At Room Temperature

At room temperature, PES and PEEK are typical engineering thermoplastics (Table 1). They are tough, strong, rigid, and have excellent load bearing properties over long periods (Fig. 2). PEEK, in particular, has outstanding resistance to dynamic fatigue (Fig. 3).

At Elevated Temperatures

As temperature increases, the mechanical properties of PES and PEEK fall. However, relative to most thermoplastics, their useful temperature service range is wide. PES can be used up to 220°C while PEEK has a limited, but useful lifetime, at temperatures in excess of 300°C.

As temperature increases, PEEK shows good retention of modulus up to its glass transition temperature (143°C). Beyond this the modulus drops sharply, but some rigidity is maintained up to its melting point (334°C). In the case of the glass reinforced grades, the level of rigidity is significant as evidenced by a heat distortion temperature of 300°C with a fiber reinforcement level of 30 percent.

PES, on the other hand, shows a rapid fall in properties beyond 200°C with very little strength or rigidity being maintained beyond 230°C. However, up to 200°C, the properties of PES show little change; dimensional stability is also excellent up to this temperature. In these regions it offers advantages over PEEK.

LONG TERM THERMAL STABILITY

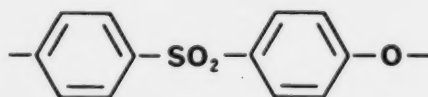
Both materials show excellent long term thermal stability. A lifetime of 50,000 hours can be expected for PES at 190°C, while for PEEK the equivalent temperature is 220°C. PES has an Underwriters Laboratory Temperature Index of 180°C and a rating in excess of 240°C is expected for PEEK.

The excellent retention of ductility on heat aging afforded by PEEK makes it a suitable candidate for high temperature wiring. Tightly wrapped PEEK coated wire offers lifetimes in excess of one week at 320°C or many years at 200°C (Table 2).

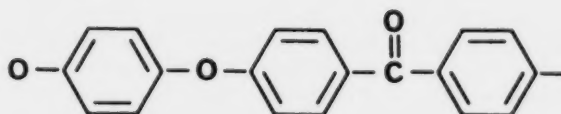
FLAMMABILITY

Increasing safety requirements have led, initially, to the demand for materials with low flammability and more recently for materials which have low smoke generation during a fire.

Both PES and PEEK admirably meet these requirements. Both materials have high Limiting Oxygen Indexes, meet Underwriters Laboratories



**Polyethersulfone
(PES)**



**Polyetheretherketone
(PEEK)**

Fig. 1. Chemical formulas of polyethersulfone (PES) and polyetheretherketone (PEEK).

PEEK Creep Rupture 23°C—Unnotched Specimens Comparison with Other Materials

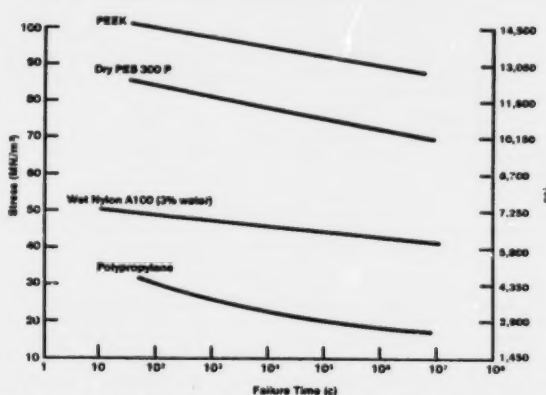


Fig. 2. PEEK creep rupture 23°C—unnotched specimens comparison with other materials.

PEEK Fatigue 23°C—Unnotched Specimens Comparison with Other Materials

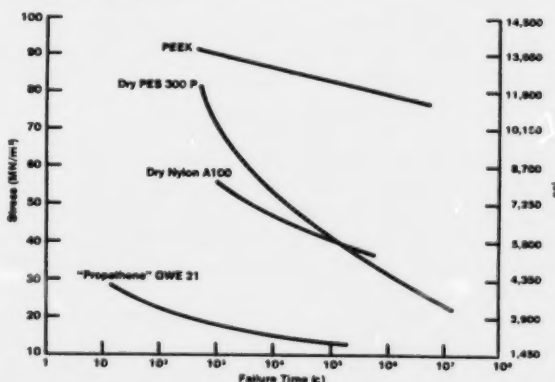


Fig. 3. PEEK fatigue 23°C—unnotched specimens comparison with other materials.

Table 2. Thermal Stability of PEEK Coated Wire (Wrapped on 6L Mandrel).

Aging Temp. C (F)	Aging Time in Days						
	1	7	14	28	63	126	253 420
320 (608)	P	P	C	—	—	—	—
280 (536)	P	P	P	P	C	—	—
240 (464)	P	P	P	P	P	P	C
220 (428)	P	P	P	P	P	P	P
200 (392)	P	P	P	P	P	P	P

Dynamic Cut-Through at 150°C—25.0 kg of PEEK Insulated Wire
P—Passed.
C—Cracked.

Table 1. Standard Properties—PES and PEEK.

Property	Units	Unfilled PES	Unfilled PEEK	20% G/F PES	20% G/F PEEK
Appearance		Light Amber Transparent	Grey/Opaque	Amber/Opaque	Grey/Opaque
Specific Gravity		1.37	1.32	1.51	1.44
Tensile Strength @ 20°C	Mn/m ²	84	93	124	123
@ 150°C	Mn/m ²	55	37	78	60
Elongation to Break @ 20°C	%	40–80	>100	3	3
Flexural Modulus @ 20°C	Gn/m ²	2.6	3.6	5.9	6.7
@ 150°C	Gn/m ²	2.5	2.2	5.8	4.3
Heat Distortion Temperature	°C	203	165	210	288

Table 3. Flammability Characteristics—PES and PEEK

Description	Method	Units	PES	PEEK	Glass Filled PES
Limiting Oxygen Index 0.016–0.125 in.	ASTM D2863	%O	33–38.5	24–35	–43
Coated Wire 24 AWG			—	40.5	—
Underwriters Laboratory Rating	UL 94	—	V-O 0.02 in.	V-O 0.06 in.	V-O 0.02 in.

Table 4. Radiation Resistance

Gamma Radiation—Ambient Temperatures			
Polymer	Dose M Rads	Method of Assessment	Conclusions
PES	0–250	Strength and ductility of film	Little effect below 250 M Rads
PEEK	0–2000	Wire wrap around 1 D Mandrel	No breakdown below 1100 M Rads

94V-O requirements and have extremely low smoke emissions (Table 3). Neither material contains flame retardant additives, nor do they contain halogens; consequently, the risk of secondary damage caused by corrosive gases, liberated in a fire, is reduced.

CHEMICAL RESISTANCE

Both PES and PEEK show extremely good hydrolysis resistance. Hot water meter parts molded from glass filled PES have been in service for a number of years at 140°C, while PEEK has been demonstrated to withstand water at 260°C (500°F) for thousands of hours.

As an amorphous plastic, PES is stress cracked by certain solvents. Relative to most amorphous plastics, the performance of PES is good, being one of the few transparent plastics not attacked by gasoline or trichloroethylene. The resistance to stress cracking is markedly improved with glass fiber reinforced grades. PES will resist most cleaning solvents but methylene chloride and the lower ketones should be avoided.

No solvent attack has been observed on molded PEEK parts, although a limited range of solvents will stress craze highly stressed PEEK coated wire. Orientation of PEEK below its melting point has been shown to overcome this problem.

RADIATION RESISTANCE

Both PES and PEEK have good resistance to hard radiation (X, β , and γ radiation). Laboratory tests show PES to be little affected by γ radiation at doses up to 250 M Rads. Electrical terminal brackets made from PES are currently in use in nuclear installations after having undergone satisfactory LOCA (Loss of Coolant Accident) testing.

Work so far suggests that the radiation resistance

of PEEK is even better, and tightly coiled PEEK coated wire samples have withstood 1100 M Rads without significant degradation (Table 4).

The UV radiation resistance of PES is not particularly good and, for prolonged outdoor exposure, black grades are recommended. The weathering resistance of PEEK is currently under evaluation. Preliminary tests show no loss of properties after one year of outdoor exposure.

COMPOSITES

The reinforcement of thermoplastics with high modulus fibers to improve strength and rigidity has been common practice for many years. However, most of the studies have been concentrated on grades with relatively short fibers suitable for injection molding. More recently, considerable interest has arisen in thermoplastics reinforced with continuous high modulus fibers such as woven carbon fiber. These composites are extremely strong and rigid and offer a weight saving over metals. The latter is of considerable interest to energy intensive industries such as aerospace and general transportation.

Both thermosets and thermoplastics have a role to play in this rapidly developing technology; the particular attractions of thermoplastics appear to be their relatively high strain to break, indefinite shelf life, and the ability to thermoform the composite/reduced fabrication labor.

Both PES and PEEK have the above attractions of thermoplastics. They also offer high strength over a wide temperature range, together with low flammability and smoke emission. PEEK, in particular, offers excellent solvent resistance. This combination of attributes is already being utilized in aerospace applications in the U.S. and Europe.

REFERENCES

1. P. J. Kimber, C. P. Smith, and T. C. Stening, "A New High Performance Thermoplastic," paper given at the SPE Antec meeting, Boston, MA, May 4–7, 1981.
2. P. J. Kimber, C. P. Smith, and T. C. Stening, pp. 86–89 (Nov. 1981), *MODERN PLASTICS*.
3. G. R. Belbin, I. Brewster, F. N. Cogswell, D. J. Hezzell, and M. S. Swerdlow, "Carbon Fiber Reinforced Polyetheretherketone: A Thermoplastic Composite for Aerospace Application," given at the 2nd Intercontinental Conference of the Society for the Advancement of Material and Process Engineering (SAMPE), Stresa, Italy, June 8–10, 1982.

Polyphenylene Ethers and Their Alloys

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Poly(phenylene ether)s (PPE) are a class of polymers which contain phenolic monomers attached via an ether linkage. Depending upon the monomer types used in the polymerization, a variety of homopolymers and copolymers can be produced. When compounded with polystyrene, these poly(phenylene ether)s combine to form single phase alloys in contrast to the separate phases obtained with most other polymer blends. Since polyphenylene ether and polystyrene are completely miscible, the alloy also has only one glass transition temperature (T_g) and behaves in a manner that is typical of single polymeric materials. By blending poly(phenylene ether)s with impact modified polystyrene at different ratios, opaque thermoplastic resins having a wide range of chemical, thermal, and mechanical properties can be manufactured. Commercially available material grades have thus been developed to meet special product requirements for flame retardancy, high impact, increased flexural and tensile strength, low creep, and good resistance to certain chemical environments. In comparison to other types of unfilled thermoplastics, poly(phenylene ether)s have a balance of properties which can overlap those of acrylonitrile-butadiene-styrene (ABS), polycarbonate, nylon, and other high performance polymers.

INTRODUCTION

Poly(phenylene ether)s (PPE) modified with impact polystyrene are thermoplastic resins presently sold under the trade names of Preverex® and Noryl®*. Because of their excellent stability at elevated temperatures, their resistance to hot water and a variety of chemical environments, and their good strength and impact balance, modified PPE materials are suitable for a broad range of applications. Some of these applications include business machine housings, appliances, automotive components, medical equipment, and communication devices.

GENERAL CHEMISTRY

Poly(phenylene ether) is the nomenclature used to describe polymers in which various types of phenolic monomers are attached by an ether linkage. The formation of the polymer by oxidative coupling requires the presence of molecular oxygen, a metal catalyst, and a solvent medium. The reaction equation for linear polymerization is shown in Fig. 1.

Within the confines of steric possibilities, any number of substitutions for the R groups are conceivable. In general, however, ring substituents for

commercially available PPE products have been limited to the hydrogen and methyl groups, with the latter occupying the 2, 3, and 6 positions (Fig. 2). With the 2 and 6 positions occupied, a linear polymer (1,4 linkage) is constructed, whereas the unsubstituted phenol can polymerize from several ring positions and results in a hard insoluble-cross-linked material having questionable utility. Low molecular weight polymers are formed when larger substituents, such as ethyl, propyl, or chlorine groups are present as side chains. Both the homo and copolymer types yield a rigid amorphous thermoplastic having a unique set of physical and chemical properties.

PPE ALLOYS

Poly(phenylene ether) polymers are recognized for their high tensile strength and modulus, resistance to many chemical environments, low water absorption, and excellent dimensional stability at elevated temperatures. On the other hand, the pure polymer does not have the impact strength, good processibility, and cost effectiveness required for many applications. To achieve a balance of these properties, PPE polymers are usually compounded with high impact polystyrenes (HIPS). The PPE/HIPS alloy, which is often referred to as a "modified PPE," has a single rigid phase comprised of the PS and PPE components which are completely misci-

* Preverex® is a registered trademark of Borg-Warner Corporation. Noryl® is a registered trademark of the General Electric Co.

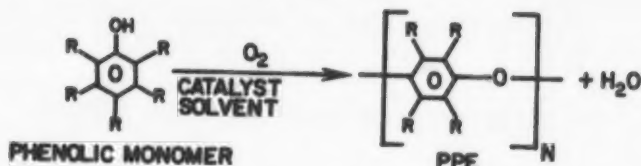


Fig. 1. Linear polymerization of polyphenylene ethers.

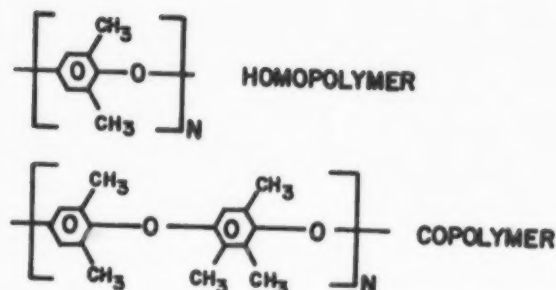


Fig. 2. Chemical structure of commercially produced PPE polymers.

ble at all ratios and exhibit a single T_g . The HIPS rubber is uniformly dispersed within the PPE and polystyrene (PS) matrix with a T_g that is characteristically lower than that of the rigid phase.

By varying the PPE/HIPS ratio, thermoplastic resins having physical properties between those for HIPS and PPE can be developed. An exception to this general rule is noted for impact performance where the alloy can have higher impact resistance than that obtained for HIPS or PPE alone. Figures 3 and 4 show the approximate shape of the curves for Izod impact, tensile strength, deflection temperature under load (DTUL), and melt viscosity as the percentage of PPE in the blend is increased.

Since PPE is inherently more flame retardant than HIPS, increasing the HIPS content will also make the material more susceptible to burning. However, additive packages are available for the development of flame retardant grades that have UL94 classifications of V-2, V-1, or V-0 at 1.6 mm (0.062 in). Whereas the basic PPE/HIPS alloy is no more resistant to ultraviolet (UV) degradation or discoloration than either of its components, stabilizers or protective coatings for severe conditions are essential when these materials are exposed to sunlight or fluorescent lights.

HIPS modified PPE will accept a variety of mineral and glass fillers. In most cases, fillers are introduced to reduce material cost or to increase the material's modulus. Filler loadings as high as 30 weight percent are possible and can result in a 2.5 fold increase in modulus. However, because of a reduction in material ductility and elongation, lower impact strength can be expected.

With the use of chemical blowing agents, structural foam versions of the PPE alloys can also be manufactured. Azodicarbonamide and sodium bicarbonate are the active ingredients in several types of foaming agents which have been used successfully to produce parts having density reductions of 10 percent to 20 percent, depending upon the

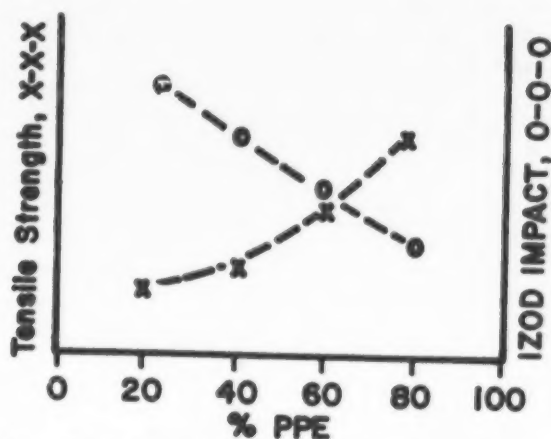


Fig. 3. Tensile strength and Izod impact versus percent PPE in PPE/HIPS alloy.

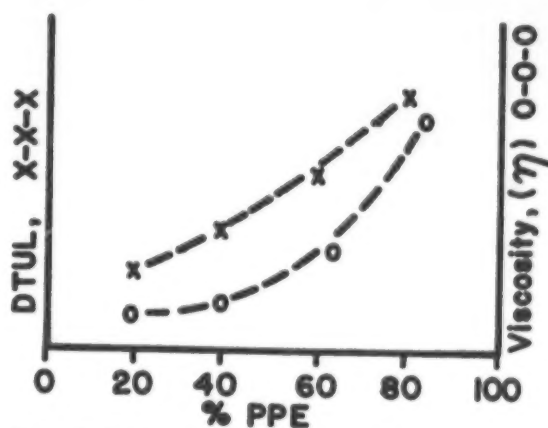


Fig. 4. Deflection temperature and viscosity versus percent PPE in PPE/HIPS alloy.

thickness of the unit. Furthermore, for nonload-bearing foamed applications, nominal wall thicknesses of 3.8 mm (.150 in) rather than the typical 6.4 mm (.250 in) are feasible.

PROPERTIES OF PPE ALLOYS

Depending upon the proportions of PPE and HIPS as well as the additive package used in any given formulation, different grades having a wide range of material properties can be manufactured. Although the property mix is unique from other polymers, certain individual traits may overlap with those of other high performance plastics (1, 2).

Strength

The ability of a material to withstand a load without yielding or breaking is determined both by

its tensile stress/strain curve and by its creep behavior. Tensile yield strength and modulus values for HIPS modified PPE at room temperature are in the range of 45.5 to 79.3 MPa (6,600 to 11,500 psi) and 2.3 to 2.6 GPa (3.4×10^5 to 3.8×10^5), respectively. These values, which are an indication of a material's short-term response, are compared in Figs. 5 and 6 to those of a number of other unfilled thermoplastics. In general, most PPE alloys have yield strengths similar to polycarbonate and acetal materials.

Creep information is used to assess a material's long-term behavior under a continuous load. An apparent or time dependent modulus can be calculated at progressive time intervals from measured specimen deflections. Figure 7 shows the creep modulus of several thermoplastics after 1000 hours at 23°C (73°F). High modulus materials are not necessarily more resistant to creep since the rate of modulus loss may be greater. PPE alloys, however, are relatively stable compared to other engineering thermoplastics.

Impact

Impact resistance is primarily a function of material ductility and tensile strength. Notched Izod

impact data, which are generally more widely available than Gardner impact values, have the additional effect of notch sensitivity superimposed upon the results. Nylon, PVC, and PC impacts are particularly influenced by notching. PPE and ABS show lesser degrees of notch sensitivity, although their unnotched impact strengths are not as great as that of PC and modified nylon. Nylons which have absorbed water are particularly tough and impact resistant. In Fig. 8, the percent of elongation for polycarbonate and certain impact modified nylons correlates well with the good Izod impact values indicated in Fig. 9. While PPE alloys do not have the impact strength of polycarbonate or ABS/PC alloys, they do outperform the molding grades of ABS, some rigid PVC's, acetal, HIPS, and the unmodified nylon types.

Heat Resistance

Commercial grades of modified PPE have a range of thermal properties that overlap those of high heat ABS and HIPS at the lower end and of polycarbonate and acetal at the upper limit. Figure 10 illustrates the comparative values for deflection

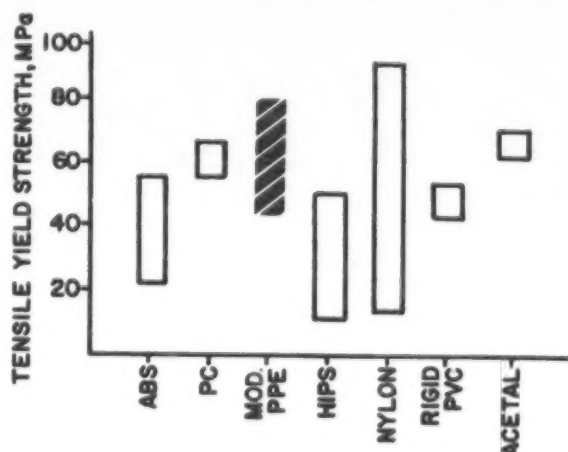


Fig. 5. Tensile yield strength of various thermoplastics.

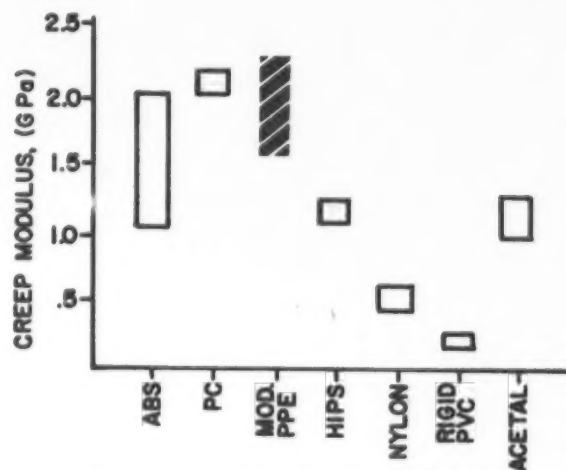


Fig. 7. Creep modulus after 1000 hours at 23°C.

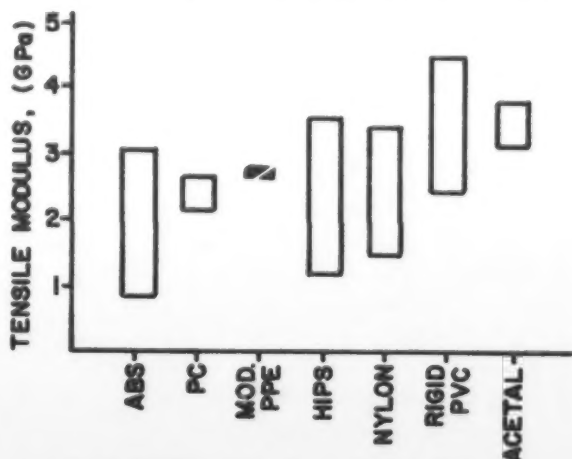


Fig. 6. Tensile modulus of several thermoplastics.

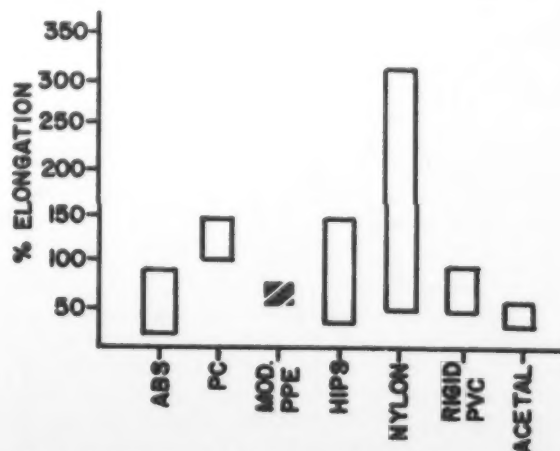


Fig. 8. The percentage of elongation of various thermoplastics.

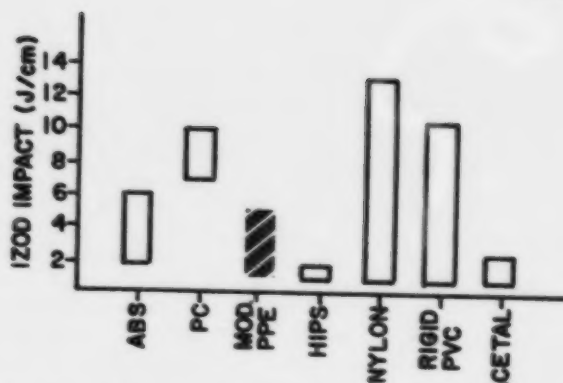


Fig. 9. Izod impact strength of notched specimens at 3.2 mm thickness.

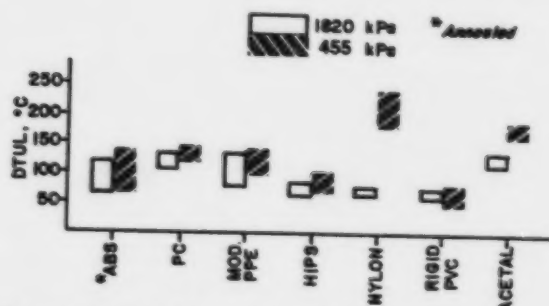


Fig. 10. Deflection temperature under load of several thermoplastics.

temperature under load (DTUL) obtained per ASTM D-648. In addition, the PPE materials do not have the load sensitivity exhibited by acetal and nylon where higher stresses cause significant losses in the deflection temperature.

Elevated temperature creep behavior is also an indication of resistance to heat. Differences in the room temperature creep rate between the PPE alloy and materials having a lower DTUL may be small. However, the gap widens when the temperature is increased since PPE is better able to maintain its load bearing ability at higher temperature.

Dimensional changes due to temperature fluctuations can be a problem in designs where part tolerances are important and where stresses can develop when dissimilar materials are joined. The coefficient of linear thermal expansion tends to be lower for the PPE alloys than for many other thermoplastics, which also contributes to its effectiveness as a plating substrate.

Moisture Absorption

Because the water absorption of PPE alloys is very low even at elevated temperatures, these materials are excellent candidates for applications requiring exposure to water or humid environments. Furthermore, HIPS modified PPE does not swell so that dimensional accuracy is also preserved. The percentage of water absorbed after 24 hours of immersion is shown in Fig. 11. The differences between materials become more pronounced for

hot water immersion since the rate and degree of absorption can increase dramatically.

The wide range of values for nylon reflects the difference between amorphous and crystalline types, with the latter having a much greater tendency to absorb water. Moderate increases in tensile strength (3.4 to 7.6 percent) and modulus (2.6 to 8.1 percent) after 60 days of immersion in 82°C (180°F) water have been noted for some grades of PPE alloys. Such changes are often an indication of material embrittlement and are probably the result of progressive leaching of material additives which act as plasticizers. However, since strength properties are maintained over time, the creep behavior of PPE alloys under humid conditions is virtually identical to its behavior in less moist air (Fig. 12).

Chemical Resistance

In general, PPE alloys are resistant to most aqueous media including acids, bases, alcohols, and detergents, but are susceptible to chemical attack by hydrocarbons, especially those which are halogenated. The severity of attack depends largely

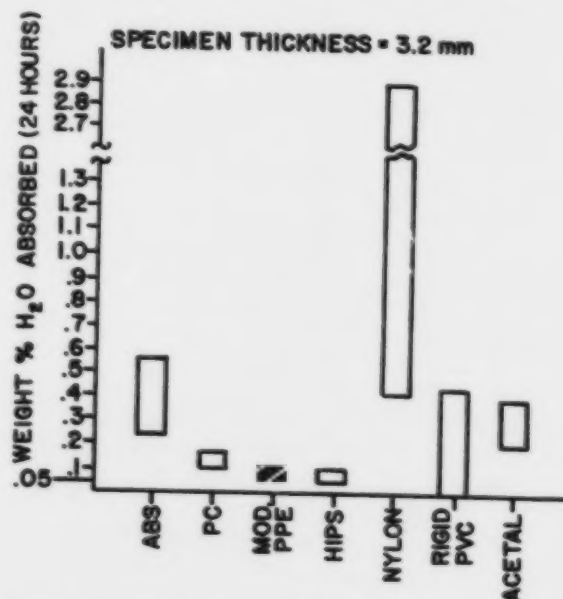


Fig. 11. The weight percentage of water absorbed after immersion for 24 hours at 23°C.

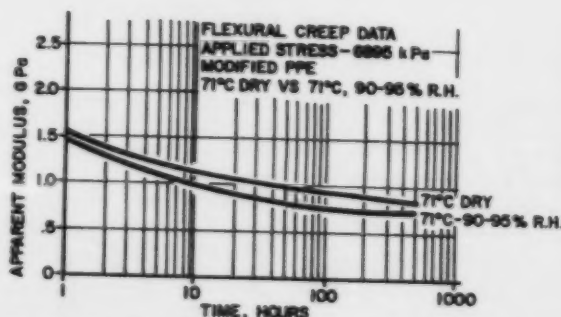


Fig. 12. The effect of humidity on the creep behavior of a PPE/HIPS alloy.

upon the degree of strain to which the material is subjected during exposure as well as to the duration of contact.

Processability

Materials having higher DTUL's are naturally more viscous and therefore require higher processing temperatures. PPE alloys are molded at stock temperatures which range from 204 to 332°C (400 to 630°F), depending upon the amount of HIPS and the various additives contained in the blend. With higher PPE content, the material flows less freely and the melt or stock temperature must be increased. Fortunately, these materials are also heat stable, making them less susceptible to polymer degradation as residence time in the barrel of the molding machine is increased. Because water absorption is low, drying prior to processing is optional for non-appearance parts. Although moisture does not affect physical properties, surface splay can still occur. Consequently, some drying (2 to 4 hours at 104°C) is recommended whenever part aesthetics are important. Mold shrinkage is 0.005 to 0.007 cm/cm, which is similar to polycarbonate but much lower than for acetal. Figures 13 and 14 compare the performances of several thermoplastics with regard to processing temperature and mold shrinkage.

Post Finishing Techniques

Although ABS is considered to be the primary substrate for plated plastic parts, PPE alloys can also be metal coated using conventional plating processes including electroplating, sputtering, and vacuum metallizing. For electroplated applications, the addition of a pre-activator step prior to the deposition of catalyst on the PPE alloy surface is the only modification required of the plating sequence used for ABS specimens. While occasionally a longer etch time may also be necessary, neither the PPE alloys nor ABS must undergo a pre-etch treatment as is the case for the polycarbonates. Modified PPE is costlier and more difficult to electroplate than ABS, but it is the preferred material when heat resistance is an important performance criterion. In addition, when the plating cycle is

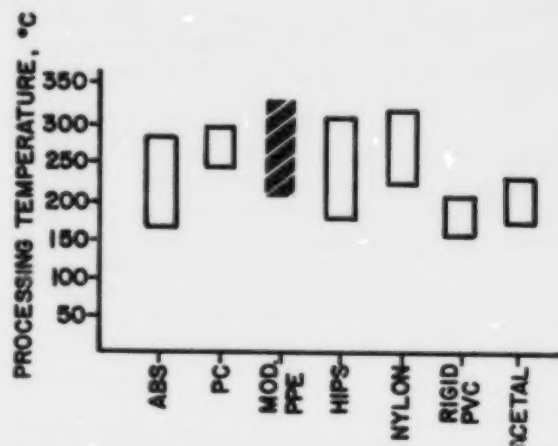


Fig. 14. Recommended stock temperatures for injection molding of various thermoplastics.

optimized for PPE alloys, good adhesion is obtained. Plated PPE alloy parts are currently being used for enclosures to shield against electromagnetic or radio frequency interference (EMI/RFI) and in the automotive, plumbing, and appliance industries.

Parts made of modified PPE can be painted, but do require a primer. Urethane, alkyd, or acrylic based paints are usually recommended. Paint adhesion is not quite as good as that achieved with ABS and polystyrene plastics, but it is comparable to the performances of nylon, poly(vinyl chloride), and polycarbonate. Decorative coatings can also be applied to the surface of PPE alloys by hot stamping.

A variety of mechanical fasteners, adhesives, and welding techniques can be used to join parts consisting of modified PPE materials (3). Both thread-cutting and thread-forming screws will work, the choice often being decided by the particular set of performance and design parameters. Inserts can be ultrasonically staked or press-fitted and expandable inserts are also acceptable. An especially convenient and economical means of attaching modified PPE components is to utilize interference fits and snap-fits in the design of a part. Integral hinges, however, require extensive flexing and are not generally feasible for stiff amorphous materials such as PPE alloys. By incorporating mechanical fasteners into the molded part, assembly operations can often be reduced both in number and complexity.

A number of adhesives are available for bonding modified PPE parts including acrylic, epoxy, hot melt, cyanoacrylate, and silicone types. The selection of a particular adhesive is highly dependent upon performance requirements and the circumstances of design. Furthermore, caution must be exercised, since adhesives can produce stress cracking in some instances. Thorough testing under actual use conditions is always recommended for any adhesive being considered.

Because of their amorphous nature, PPE alloys are good candidates for solvent welding, as are the ABS, polycarbonate, polystyrene, and polyvinyl chloride thermoplastics. Crystalline polymers such

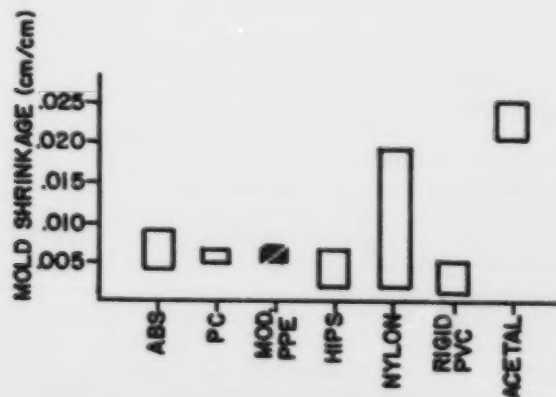


Fig. 13. Mold shrinkage of various thermoplastics.

as nylon and acetal are not joined by this method. Ultrasonic heat and vibrational welding techniques also work well with the modified PPE materials.

SUMMARY

Alloys of poly(Phenylene ether)s are viable thermoplastic materials for present and future applications requiring the specific qualities of high strength, heat resistance, and moisture resistance. A selection of flame retardant grades which maintain these excellent characteristics is also available. Because the polymer blend will readily accept a variety of fillers, additives, and foaming agents, the

property range can be extended to satisfy a diversity of special performance needs. These modified PPE materials compete successfully against other engineering thermoplastics in many markets including electronics, business machine, automotive, appliance, plumbing, medical, and communications.

REFERENCES

1. "Plastics . . . A Desk-Top Data Bank®," 6th Edition, pgs. A-15 to A-28, The International Plastics Selector, Inc., San Diego, (1983)
2. *Mod. Plast. Encycl.* 60 (10A), 469-728 (1983-1984)
3. R. D. Beck, "Plastic Product Design," 2nd Edition, pp. 200-246, Van Nostrand Reinhold Company, New York (1980)

Permeability Barriers by Controlled Morphology of Polymer Blends

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Melt fabricated plastic articles with improved solvent and vapor barrier properties are of great need in the packaging industry. Various techniques, such as coextrusion, surface treatments, and coatings, are being employed currently towards this objective. Present work has identified a unique polymer blend approach to impart solvent and gas barrier properties to a polyolefin material. This involves incorporation of small amounts of a modified nylon barrier material, and processing under controlled conditions, in single step blowmolding or other extrusion processes. The unusual barrier effects obtained at small concentrations of the barrier material are obtained by the controlled morphology of the dispersed phase and optimum formulation of the ingredients.

INTRODUCTION

Polyolefins such as polyethylene and polypropylene are the materials of choice for packaging many fluids. These are easily processible, economical, safe, and uniquely suited for containing aqueous materials and a limited number of organic liquids. However, solvents and vapors such as hydrocarbons and chlorinated solvents have high permeability through polyolefins.

Various techniques to adapt low cost polyolefins to contain more aggressive solvents and vapors are known. These, in general, involve incorporation of a layer of a resistant polymer next to the more permeable polymer. Examples are application of surface coatings from polymers such as polyvinylidene chloride, acrylonitrile, nylon, etc. depending on the permeant. These involve applications from a solvent, dispersion, or melt coextrusion techniques. Novel techniques of modifying the surfaces by highly reactive vapors are also available (1, 2). Each one of these techniques has its own advantages and disadvantages.

Combinations of two or more layers of incompatible thermoplastic polymers in continuous layers need multiple extrusion systems and appropriate adhesives and additional extruders for their applications. While such technology has attained a high degree of sophistication in extrusion of films and sheets, their application to container manufacture by blowmolding is still restricted to special cases.

Combinations of a thermoplastic barrier material with a lower cost matrix material, which then could be processed in a single step operation, if feasible,

could have significant advantages in versatility and cost. However, in homogeneous blends wherein small amounts of a thermoplastic barrier material is homogeneously distributed, generally only modest improvement in the permeability barrier can be obtained. This reduction arises because of the longer path length that the permeant molecule has to travel, compared with the unmodified matrix polymer, and can be calculated using expressions derived by Nielsen (3), and Barrer, *et al.* (4) analogous to the treatment of conductivity by Maxwell (5, 6) and as discussed by Hopfenberg and Paul (7) and the references cited therein.

EXPERIMENTAL

The various barrier components were dry blended with pellets of polyethylene and the "dry blend" blowmolded or fabricated into films by using continuous extrusion machines, under different mixing/shear conditions. These articles were then tested for permeability effects by exposing them to solvents or mixture of solvents and determining the losses by weighing. The tests were carried out generally at ambient conditions, or at 60°C. Cross-sections of the fabricated parts, e.g. walls, were analyzed by optical microscopy. The nylon specimens were also dyed blue for better definition.

RESULTS AND DISCUSSIONS

Incompatible polymers, when blended together, result in poor dispersions in which the dispersed phase is very large and lacks adhesion to the matrix (Fig. 1). This becomes extremely important when



Fig. 1. Polyethylene-nylon blend (without compatibilizer).

one wants to modify a polyolefin for permeability barrier properties by blending with a barrier polymer such as nylon, polyvinylidene chloride, or polyacrylonitrile. To a great extent, these blends can be improved by incorporating a surfactant or compatibilizer or interfacial agent. Such blends, especially in the cases of polyolefins and nylon, are well known in the literature (8) which describes homogeneous blends wherein the dispersed phase is homogeneously distributed in the matrix phase. Such technology is the basis of toughening of thermoplastics (e.g. toughened nylon) (9) as well. Figure 2 shows the small particles of nylon dispersed in the polyolefin matrix in such homogeneous blends.

For transport properties such as permeability, the continuous phase has the predominant effect. Homogeneous blends of a permeable thermoplastic material such as the matrix and small amounts of a thermoplastic barrier material are usually still very permeable until there is a substantial volume fraction of the latter.

This work pertains to the development of a unique morphology of polymer blends and its utilization, and a method to impart various permeability barriers to low cost polyolefins using small amounts of a barrier polymer. This system is exemplified here by the use of a nylon based "concentrate" for addition to polyethylene and melt fabrication of permeability resistant articles.

A blend of linear high density polyethylene (HDPE) and 20 percent nylon, when subjected to normal processing under good mixing conditions without any compatibilizing additives, gives blends which show gross incompatibility and break easily, as would be expected. A similar nylon with a composition modified for compatibility and processed using conventional mixing techniques affords arti-

cles which are very tough and have good physical properties. While these are good candidates for molding applications, hydrocarbon permeability tests indicate that these afford only about 20 percent better improvement over control high density polyethylene (Table 1) (Fig. 3).

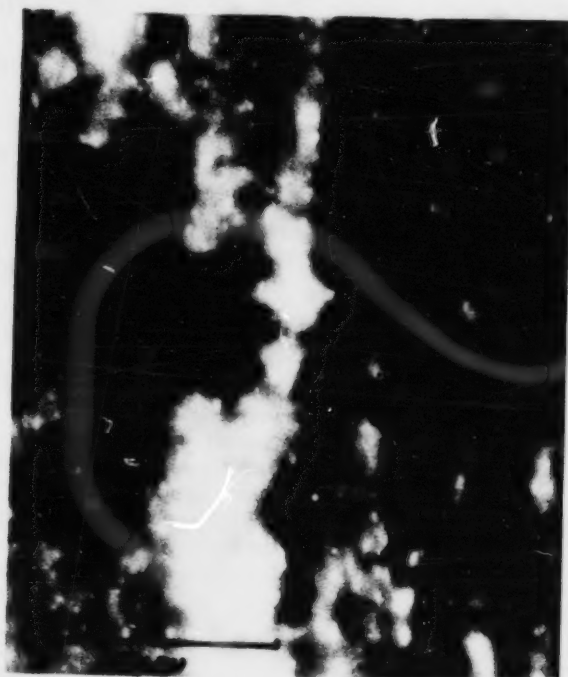


Fig. 2. Homogeneous polyethylene-nylon blend (compatibilized).

Table 1. Homogeneous Polyethylene-Nylon Blends.

Composition	A	B	C
Yield Strength, MPa	26.8	—	34.4
Tensile Strength, MPa	27.2	23.7	34.4
Elongation, %	300	—	100
Impact, Notched Izod, J/M	NB	123	NB
Hydrocarbon Barrier Factor	1	—	0.8

A = High Density Polyethylene.

B = High Density Polyethylene and 20 percent Nylon.

C = High Density Polyethylene and 20 percent Nylon & Compatibilizer.

NB = No break.

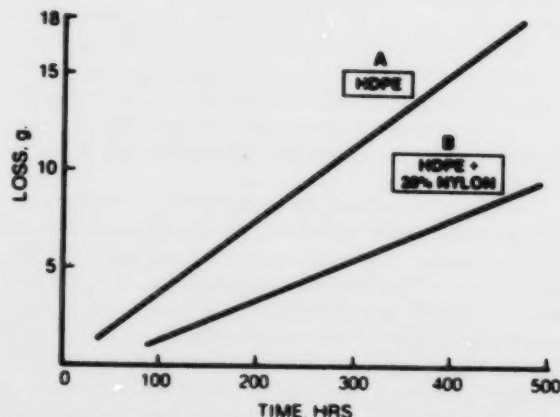


Fig. 3. Hydrocarbon permeability in 16 ounce blowmolded bottles.

In studying the morphology of these systems as a function of the size and shape of the nylon particles, it was discovered that the same blend of materials, when processed in an extruder system under controlled processing conditions where the melted nylon particles are prevented from becoming tiny droplets, afford quite different permeability properties.

Figure 4 shows permeability of hydrocarbons in containers fabricated under various conditions. The polyethylene container typically loses 1 g of hydrocarbon per day. A homogeneous, compatibilized polyethylene-nylon (20 percent) blend, in similar containers, shows modest improvements in permeability barrier. However, the containers made under the modified conditions offer significantly improved barrier properties over the control polyethylene.

When processed ideally, a blowmolded container with substantially improved permeability barrier properties can be made. Permeability losses of selected solvents in 16 oz. blowmolded containers are given in Table 2. Examples of chlorinated solvents, hydrocarbons, esters and ketones, and alcohols are given. The nylon system offers good performance

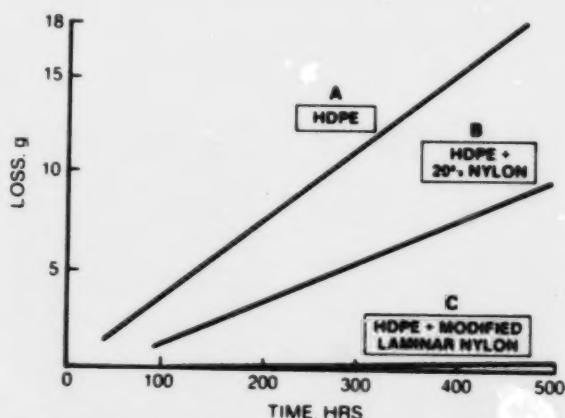


Fig. 4. Hydrocarbon permeability in laminar walled PE-nylon barrier bottles.

Table 2. Permeability, Loss (g.), in 4 oz. Blowmolded Containers.

Solvent	HDPE	HDPE-Nylon Laminar Container	Permeability Factor
Toluene	5.5	0.04	138
Heptane	3.0	0.07	43
Hexane	4.4	0.10	44
Naphtha	2.0	0.07	29
O-Dichlorobenzene	1.6	0.02	80
Trichloroethane	0.56	0.02	28
Tetrachloroethane	12.1	0.10	121
Methylene Chloride	7.6	3.6	2
'Freon' F-113	0.05	0.03	2
Ethyl Acetate	0.30	0.03	10
Methyl Ethyl Ketone	0.15	0.03	5
Acetone	0.10	0.04	2
Methanol	0.03	0.07	2

* Filled containers
 = 23°C
 = 21 days duration

in the first two categories and modest improvement for ketones and esters. Low permeability losses for tetrahydrofuran, as well as some solvent based paints and various commercial products, are given in Tables 3 and 4.

While polyamides are not the material of choice for oxygen barrier, these do, when processed under these conditions, afford modest oxygen barrier improvement as well. Table 5 shows an eight-fold improvement in this property.

EFFECT OF NYLON CONCENTRATION ON PERMEABILITY BARRIER PROPERTIES

The permeability data presented earlier pertains mostly to compositions containing 18 or 20 percent of the barrier nylon component. The efficient use of the barrier concentrate in this manner gives us a spectrum of properties based on the concentration. Figure 5 describes the effect on permeability of xylene in containers made from blends of high density polyethylene and lower amounts of the nylon component. While optimum permeability barrier properties are obtained at 18 percent, modest to good properties are obtained at concentrations of 5 to 10 percent.

MORPHOLOGY OF POLYETHYLENE-NYLON BLENDS

As mentioned earlier, homogeneous blends of polyethylene and small amounts of nylon afford little improvement in barrier properties. However, the modified processing techniques, with the appropriate selection of the nylon and compatibilizer systems, yield a structure that has remarkable impermeability. This becomes evident as we study the distribution of nylon in the polyethylene matrix.

Table 3. HDPE—Nylon Laminar Containers Permeability Loss.

Tetrahydrofuran:	0.97% Per Year
Dulux® Enamel Paint:	0.2% Per Year
Paint Thinner:	1.0% Per Year

Table 4. Permeability (Loss, Percent Annual) of Solvent Containing Autocare Products in HDPE—Nylon Laminar Containers.

	PVC	HDPE	PAN	HDPE—Nylon Laminar Container
Gas Booster®	Softens	94%	Negligible	0.13%
Car Wax	1.5	10%	2.2%	0.22%
Prep-Sol®	Softens	5%/WK	2.4%	0.24%
Brake Fluid	N/A	N/A	1-5%	Negligible at 120°F

PVC = Poly(vinyl chloride).
 HDPE = High Density Polyethylene.
 PAN = Acrylonitrile co-polymer, produced by Viatron Corp.

Table 5. Oxygen Permeability HDPE-Nylon Laminar Bottles (16 oz.).

	CC 02/24 Hrs
HDPE	0.73
HDPE/Modified Nylon	0.09

Figure 6 shows the section of the wall of a container blowmolded from the above material system, under conditions selected to give good barrier properties. The nylon material is distributed not as a homogeneous, uniform blend, but is distributed as multiple layers or platelets along the wall thickness. Optimization of such morphology contributes to outstanding barrier properties, and is critical for attainment of good barrier properties at small load-

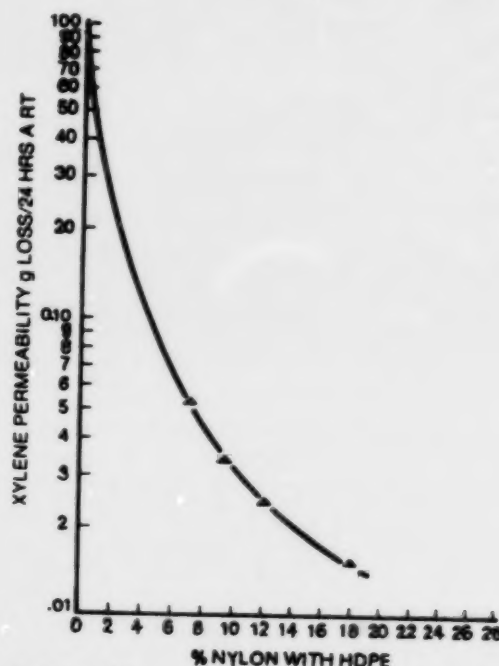


Fig. 5. Permeability as a function of nylon concentration, in laminar walled containers.



Fig. 6. Cross-section of wall of laminar walled PE/nylon container.

ings of the barrier material. This morphology can also be demonstrated by other techniques.

Figure 7 shows the views of a section of the wall, using a hot stage microscope. As the temperature is increased, even after the melting point of the polyethylene, the platelet shape of nylon is retained.

Some theoretical calculations can be made regarding the barrier properties of a composite of this material. Calculations (7, 10) can be made using Robeson's equation for permeability through a composite of two layers of nylon and polyethylene. Equation 1 gives the permeability of a composite of two layers.

$$\frac{1}{P_c} = \frac{\phi_1}{P_1} + \frac{\phi_2}{P_2} \quad (1)$$

For a homogeneous system, the corresponding expression is given by Eq. 2.

$$\bar{P}_c = \bar{P}_m \left[\frac{P_d - 2P_m - 2\phi_d (P_m - P_d)}{P_d + 2P_m + 2\phi_d (P_m - P_d)} \right] \quad (2)$$

where $\bar{P}_c$ = Permeability of the composite.

$\bar{P}_m$ = Permeability of the matrix.

P_d = Dispersed phase.

ϕ_d = Volume fraction of dispersed phase.

ϕ_1 = Volume fraction of Phase 1.

ϕ_2 = Volume fraction of Phase 2.

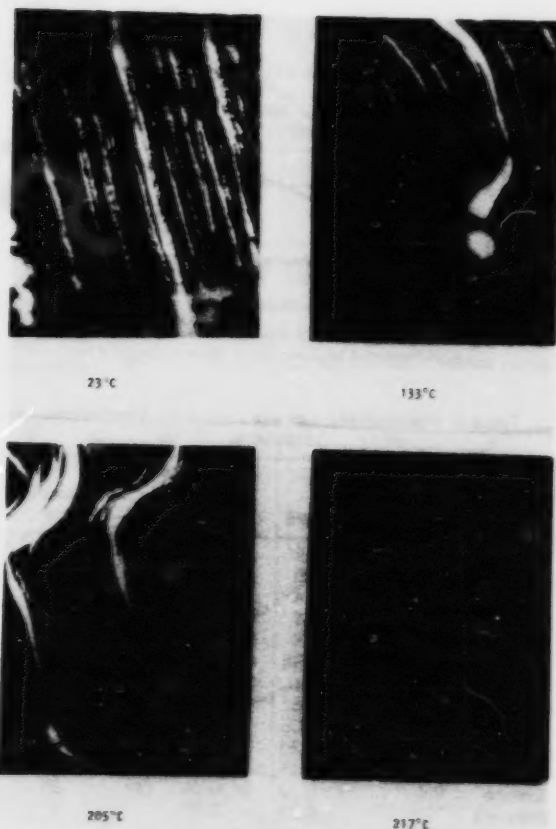


Fig. 7. Photomicrograph of HDPE/Nylon laminar bottle walls 80x.

If one assumes that polyethylene is the continuous phase (Fig. 8), a substantial volume of nylon will be needed for reduction of permeability. A composite structure, made from continuous layers of polyethylene and nylon, should have good permeability barrier.

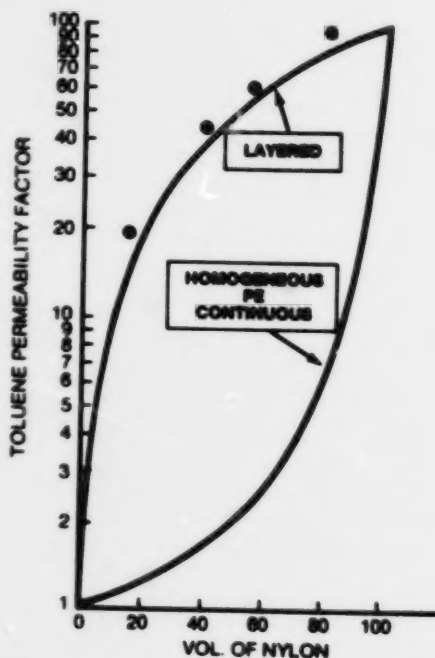


Fig. 8. Theoretical and experimental values of permeability versus dispersion mode.

In the case of the PE-nylon laminar system processed in a laminar process, one gets properties approaching that of a composite, of the distinct layers of the polyolefin and nylon.

CONCLUSIONS

Presented here is a unique system for barrier control, using a simple one-step extrusion process involving a relatively low cost polyolefin resin as the matrix and small amounts of a thermoplastic barrier material. The unusual properties are obtained by the use of the controlled laminar morphology of the dispersed nylon phase.

REFERENCES

1. L. J. Hayes and D. D. Dixon, *J. Appl. Polym. Sci.*, **23**, 1907 (1979).
2. G. P. Ziemba, L. S. Thomas, C. P. Parsons, and R. A. Hollo, *Plas. Surf. Transp., Natl. Tech. Conf., Soc. Plas. Eng.* (Pub. 1974) p. 105-107 SPE., Greenwich, Conn. (1974).
3. Nielsen, L. E., *J. Macromol., Sci A I*, **292** (1967).
4. R. M. Barrer, J. A. Barrie, A. S. Rogers Michaels, and H. J. Bixler, *J. Polym. Sci.* **50**, 413 (1961).
5. J. C. Maxwell, "Electricity and Magnetism," London Clarendon Press, (Reprint, 2nd Edition, Vol. 1.), New York, Dover (1904).
6. References cited in "Polymer Blends and Composites," by J. A. Manson and L. H. Sperling, Plenum Press, New York (1976).
7. D. R. Paul and S. Newman, "Polymer Blends," (Vol I, Chapter 10 (H. B. Hopfenberg and D. R. Paul), Academic Press, New York (1978).
8. A. D. Armstrong, U.S. Pat. 3,373,222 (1968). R. B. Mesrobian, P. E. Sellers, D. Ademaitis, U.S. Pat. 3,373,224 (1968).
9. B. N. Epstein, U.S. Pat. 4,174,358 (1979).
10. L. M. Robeson, G. A. Nosha, and M. Patzner, *Die Angew. Makromol Chem.* **29/30**, 47 (1973).

Two and Three Component Interpenetrating Polymer Networks

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Two and three component interpenetrating polymer networks (IPNs) have been prepared from polyurethanes, epoxy resins, and acrylic copolymers using the simultaneous technique (SIN). These materials exhibited a variety of morphologies and properties dependent on the types of polymer, molecular weight of precursors, presence of charge groups, and presence of intentional grafts between the component polymer networks. In general, decreasing molecular weight of prepolymers, presence of intentional grafts, and presence of charge groups of opposite charge resulted in increased homogeneity (interpenetration). In addition, increased homogeneity resulted in enhanced mechanical properties.

INTRODUCTION

Interpenetrating polymer networks (IPNs) (1 to 6) are novel blends of crosslinked polymers containing essentially no covalent bonds, or grafts, between them. True IPNs are also homogeneous mixtures of the component polymers.

IPNs possess several interesting characteristics in comparison to normal polyblends. Formation of IPNs is the only way to intimately combine crosslinked polymers, the resulting mixture exhibiting (at worst) only limited phase separation. Normal blending or mixing of polymers results in a multiphase morphology due to the well-known thermodynamic incompatibility of polymers. However, if mixing is accomplished simultaneously with crosslinking, phase separation may be kinetically controlled by permanent interlocking of entangled chains.

The present studies in IPNs have encompassed a variety of areas, including molecular weight effects, crosslinking effects and the effects of charge groups and intentional grafts on the morphology and properties, pseudo-IPNs, and three component IPNs. The polymers studied have been polyurethanes, acrylic polymers and copolymers, and epoxies.

EXPERIMENTAL

Preparation

Preparation of all the various IPNs which will be discussed in this paper followed the same basic procedure. The urethane prepolymer was mixed with a prepolymer syrup of acrylic (~15 to 20 percent conversion) or with an epoxy resin, together with chain extenders, crosslinking agents, and catalysts. This was then mixed and sheet specimens prepared by casting in aluminum molds and curing at 100°C on a platen press. In some cases, solvents were used to facilitate mixing. In these instances, the solvents were removed by allowing the mold to remain open overnight.

The urethane prepolymers were prepared by reacting a polyol with excess diisocyanate at 60 to 80°C (under dry conditions in nitrogen) until the isocyanate content reached the desired level, as determined by the di-n-butylamine titration method (7). All polyols were first dried at 80°C under vacuum for 16 hours.

The acrylic prepolymers were prepared by heating the washed and distilled monomer at 60 to 80°C using benzoyl peroxide as catalyst. Cross-linking was accomplished by curing with ethylene glycol

dimethacrylate or trimethylolpropane trimethacrylate.

In the case of pseudo-IPNs, the appropriate cross-linking agent (triol or dimethacrylate) was omitted from the formulation.

Characterization of Polymers

The ultimate mechanical properties were determined according to standard ASTM procedures. Dynamic mechanical properties were determined on a Rheovibron Dynamic Viscoelastometer Model DDV-II-C, with a temperature scan from 200 to 450K (not exceeding a scanning rate of 1 deg/min.). Glass transition temperatures were determined from these measurements as well as by differential scanning calorimetry (Perkin Elmer DSC-II).

Samples were prepared for scanning electron microscopy (SEM) by freeze-fracturing in liquid nitrogen and applying a gold coating of approximately 2000 nm. Micrographs were obtained using a Philips scanning electron microscope Model SEM 505.

RESULTS AND DISCUSSION

Polyurethane (PU)-Poly(Methyl Methacrylate) (PMMA) IPNs

In order to further study the effects of interpenetration, the molecular weight of the prepolymer was varied by changing the NCO/OH ratio in the prepolymers, as well as employing polyols of varying molecular weight (650, 1000, and 2000). In addition, charge groups were also introduced into the component polymers in order to determine the effects of specific interaction between component polymers on the morphology and physical properties of the IPNs. It was anticipated that groups of opposite charge on the component polymers should increase their compatibility. Curing of the polyurethane was accomplished with 4,4'-methylene bis-(2-chloroaniline) (MBCA). The isocyanate employed was 4,4'-diphenylmethane diisocyanate (MDI). IPNs composed of 80 and 90 percent PU were prepared.

The formulations of various urethane prepolymers are shown in Table 1. The glass transitions of the IPNs and the component polymers are shown in Tables 2 and 3. These results indicate that the most compatibility is evidenced when prepolymers were based on either low molecular weight polyol, or increased NCO/OH in the prepolymer. This may be deduced from the greater T_g (i.e., closer to $T_g(A)$) as well as the presence of a second T_g in the

highest molecular weight prepolymer materials (PU-VII, PU-III, PU-IV, and PU-V in Tables 2 and 3). The scanning electron micrographs (figures not shown) agree with this behavior, i.e. the most homogeneous looking IPNs are those prepared from the lower molecular weight prepolymers. The mechanical properties of these IPNs (Tables 4 and 5) show that the best strength properties are exhibited by the most compatible IPNs.

The reasons for increased compatibility and mechanical properties with IPNs prepared from lower molecular weight prepolymers is undoubtedly due to the increased compatibility of the initial prepolymer mixture (due to the lower molecular weight). In addition, an increase in NCO/OH in the prepolymer will result in a more highly crosslinked polyurethane-urea which is also conducive to interpenetration (over the range studied) (see Table 6).

Introduction of charge groups into the polymers also resulted in increased interpenetration, as evidenced by glass transition behavior (Table 7) and electron microscopy (figures not shown). Increased compatibility again resulted in enhanced mechanical properties (see Tables 8 and 9). The charge groups undoubtedly provide for specific interactions between the component polymers which could reduce the enthalpy of mixing to result in an overall reduction of the free energy of mixing (entropy will not be affected by the presence of charge groups).

Similar experiments with polyurethane-epoxy IPNs yielded the same results, i.e. increased concentration of charge groups resulted in increased interpenetration and enhanced mechanical properties. In addition it was found that intentional grafting between polymers yielded similar results, i.e. increased interpenetration and enhanced mechanical properties. The grafts undoubtedly result in increased compatibility, similar to the effects of charge groups.

Three Component IPNs

Morphology

Tables 10 and 11 show the compositions of the individual components and the ternary IPN. The mechanical spectra of the Type-III IPNs (opposite charge) are shown in Fig. 1. As the concentrations of epoxy and acrylic polymers were increased, T_g (peak in E'' versus T) shifted to the right (higher temperature) and gradually broadened. The three-component IPN containing 70 percent polyure-

Table 1. Polyurethane Prepolymers of Different NCO Percent and Molecular Weight of Polyols.

Description	Composition	NCO/OH	NCO% (Theory)	NCO% (Experiment)
PU-I	Polymeg 1000* + MDI	2.76	8.75	8.63
PU-II	Polymeg 1000* + MDI	2.49	7.7	7.62
PU-III	Polymeg 1000* + MDI	2.25	6.7	6.61
PU-IV	Polymeg 1000* + MDI	2.00	5.6	5.52
PU-V	Polymeg 1000* + MDI	1.86	4.95	4.84
PU-VI	Polymeg 650 + MDI	1.62	4.95	4.83
PU-VII	Polymeg 2000 + MDI	2.49	4.95	4.84

* Poly(1,4-oxybutylene) glycol.

thane exhibited the broadest glass transition. Its loss modulus peak contained a small shoulder, perhaps indicating slight phase separation with two, or even three T_g s superimposed on one another. When

Table 2. Effect of NCO/OH Ratios in PU Prepolymers on the Glass Transition Temperatures (by DSC).

Composition of Materials	NCO/OH of PU Prepolymer	$T_g(D)^{\circ}K$ (by DSC)	$T_g(A)^{\circ}K$ (Calc)
PU-I/PMMA (90/10)	2.76	253	255.4
PU-II/PMMA (90/10)	2.49	249	253.6
PU-III/PMMA (90/10)	2.25	245 (267)	250.9
PU-IV/PMMA (90/10)	2.00	242 (253)	249.1
PU-V/PMMA (90/10)	1.86	238 (260)	246.4
PU-I	2.76	247	—
PU-II	2.49	245	—
PU-III	2.25	245	—
PU-IV	2.00	240	—
PU-V	1.86	237	—
PMMA	—	331	—

Table 3. Effect of Molecular Weight of Polyols in PU on the Glass Transition Temperatures (by DSC).

Composition of Materials	MW of Polyol in PU	$T_g(D)^{\circ}K$ (by DSC)	$T_g(A)^{\circ}K$ (Calc)
PU-VI/PMMA (90/10)	650	245	251.8
PU-V/PMMA (90/10)	1000	239	246.4
PU-VII/PMMA (90/10)	1904	200 (269)	214.9
PU-VI 100%	650	243	—
PU-V 100%	100	237	—
PU-VII 100%	1904	202	—
PMMA 100%	—	331	—

Table 4. Effect of NCO/OH in the PU Prepolymers on the Mechanical Properties.

Composition of Materials	NCO/OH of PU Prepolymer	Tensile Strength MPa	100% Modulus MPa	300% Modulus MPa	Elongation (%)	Hardness (Shore A)
PU-I/PMMA (90/10)	2.76	57.1	25.2	37.7	640	96
PU-II/PMMA (90/10)	2.49	49.6	20.9	32.3	610	95
PU-III/PMMA (90/10)	2.25	37.6	13.6	19.7	670	93
PU-IV/PMMA (90/10)	2.00	34	10.5	15.0	765	91
PU-V/PMMA (90/10)	1.86	31.8	9.9	13.6	835	88

Table 5. Effect of Polyols Molecular Weight in the Polyurethane on the Mechanical Properties.

Composition of Materials	MW of Polyol in PU	Tensile Strength MPa	100% Modulus MPa	300% Modulus MPa	Elongation (%)	Hardness (Shore A)
PU-VI/PMMA (90/10)	650	50.4	12.2	21.5	650	92
PU-V/PMMA (90/10)	1000	31.8	9.9	13.6	885	88
PU-VII/PMMA (90/10)	1904	26.5	7.28	9.7	1135	85

Table 6. Composition of Polyurethanes, Polymethacrylates, and IPNs with Charge Groups.

Description	Materials	Composition
PU	Polyurethane	PTMO 1000, MDI and MBCA NCO/OH = 2/1, NCO/NH ₂ = 1.05
NPU	Tertiary amine-containing polyurethane*	PTMO 2000, MDI, BHPA* and MBCA, NCO/OH = 2/1, NCO/NH ₂ = 1.05
PMMA	Poly(methyl methacrylate)	Prepolymer solution of MMA
P(MMA-MAA)	Poly(methyl methacrylate-methacrylic acid)	Prepolymer solution of MMA and MAA at different ratios of MMA/MAA (4/1, 6/1, 8/1, 10/1)
IPN-I	PU/PMMA	PU/PMMA = 80/20
IPN-II	NPU/P(MMA-MAA)	NPU/P(MMA-MAA) = 80/20

* Bis-(2-hydroxypropyl) amine mixed with PTMO 2000 to achieve an average molecular weight of 1000.

the concentrations of epoxy and acrylic polymers were increased to a combined total greater than 30 percent, sharp E'' peaks were again observed. We would like to suggest that phase inversion occurred near the composition containing 70 percent polyurethane.

The mechanical spectra of four types of three-component polymer alloys having the composition PU/PE/PA = 80/10/10 are shown in Fig. 2. The G-IPN exhibited a very sharp peak. This implies that the degree of interpenetration between the BrPU-IEM grafted network and the epoxy network was high, with excellent molecular mixing. In the absence of covalent chemical bonding between the polyurethane and methacrylate polymers and a replacement of such bonding with weak physical attractions between opposite charge groups in the constituent networks, the E'' peak was broadened. This may be seen in Fig. 2 by comparing the relative breadths of the C-IPN and Type-III glass transitions. Obviously, secondary physical attractions are much weaker than primary covalent bonds, and as a result the degree of molecular mixing was decreased. When these weak physical attractive forces were eliminated in the Type-II IPN (similar charge), the E'' peak observed was even broader, and the molecular mixing was further decreased. Finally, the PDIPN containing linear polyurethane and acrylic polymers exhibited two distinct T_g s. However, since the epoxy was crosslinked, an entanglement of the linear polyurethane and methacrylate

chains with the epoxy network was possible, and the two T_g s were relatively close to one another (see Table 12). The morphological changes observed in the mechanical spectra are accompanied by similar changes in mechanical properties.

The electron microscopy results (micrographs not shown) revealed morphologies consistent with the T_g studies.

Table 7. Effect of Charge Groups on the T_g s of IPNs by DSC.

Composition	MMA/MAA (mole)	-COOH% (mole)	$T_g(D)^{\circ}K$ (DSC)	$T_g(A)^{\circ}K$ (Calc)
PU (100%)	—	—	240	—
NPU (100%)	—	—	242	—
PMMA (100%)	—	—	331	—
P(MMA-MAA) (100%)	—	—	357	—
P(MMA-MAA) (100%)	4/1	20	351	—
P(MMA-MAA) (100%)	6/1	14.3	348	—
P(MMA-MAA) (100%)	8/1	11.3	345	—
IPN-II (80/20)	10/1	9.0	263	265
IPN-II (80/20)	4/1	20	260	263.8
IPN-II (80/20)	6/1	14.3	258	263.2
IPN-II (80/20)	8/1	11.3	254	262.6
IPN-I (80/20)	10/1	9.0	242 (253)	249.1

Ultimate Mechanical Properties

The mechanical properties of the polyurethane, epoxy, and acrylic homopolymers are listed in Table 13. Crosslinked epoxy (0510) exhibited the highest tensile strength and lowest elongation at break due to the high crosslink density and rigid structure.

As shown in Table 14, the Type-V G-IPN (graft-IPN) exhibited the best mechanical properties due to the existence of covalent chemical bonding between the IEM and BrPU networks. The Type-III IPNs (opposite charge) also exhibited improved properties over the other IPN types. Presumably, weak physical ionic interactions brought about by the charge groups in the constituent networks and grafts between the components helped to compatibilize the polymers. This undoubtedly decreased the degree of phase separation and aided in the formation of IPNs with enhanced properties and more homogeneous morphologies. The Type-II IPN (similar charge) showed improved properties over the Type-I IPN (no charge). The high concentration of tertiary amine groups in the Type-II IPN helped to match the crosslinking rates of the three

Table 8. Effect of Charge Groups on Mechanical Properties of IPNs.

Composition	MMA/MAA (mole)	Tensile Strength MPa	100% Modulus MPa	300% Modulus MPa	Elongation (%)	Hardness (Shore A)
PU (100%)	—	30.3	7.5	10.9	9.0	90
NPU (100%)	—	38.2	11	16.9	650	92
IPN-I (80/20)	1/0	38.2	10.8	18.7	557	92
IPN-II (80/20)	4/1	49.8	11.7	20.5	685	91
IPN-II (80/20)*	4/1	46.8	11.1	20.0	695	92

* Prepolymer of MMA and MAA was prepared in the absence of a chain transfer agent (CCl_4).

Table 9. Effect of Charge Groups Concentration in Methacrylate Polymers on Mechanical Properties of IPNs.

Composition	MMA/MAA (mole)	-COOH* (%)	Tensile Strength MPa	100% Modulus MPa	300% Modulus MPa	Elongation (%)	Hardness (Shore A)
NPU	—	—	38.2	11.0	11.7	650	92
IPN-II (80/20)	4/1	20	49.8	11.7	22.1	685	91
IPN-II (80/20)	6/1	14.3	43.7	13.8	21.6	633	91
IPN-II (80/20)	8/1	11.1	44.3	12.8	21.2	643	91
IPN-II (80/20)	10/1	9	40.9	13.1	20.5	623	92
IPN-I (80/20)	—	—	40.2	8.3	14.1	720	88

* Theoretical calculation from MMA/MAA mole ratios.

Table 10. Descriptions of Polyurethane, Epoxy, and Acrylic Homopolymers.

Sample Abbreviation	Sample Type*	Composition	Diols (in Polyurethanes)**	Charge Group Concentration Percent		
				Polyurethane	Epoxy	Acrylic
CU	i	PU 100%	A + 1, 4 BD	—	—	—
NPU	i	PU 100%	A + MDEA	0.48 (—N—)	—	—
BrPU	i	PU 100%	A + DBBD	2.96 (—Br)	—	—
LBrPU	ii	LU 100%	A + DBBD	2.96 (—Br)	—	—
0510	iii	PE 100%	—	—	5.40 (—N—)	—
BMA	iv	PA 100%	—	—	—	—
DMA	iv	PA 100%	—	—	—	8.92 (—N—)
LDMA	v	LA 100%	—	—	—	8.92 (—N—)

* i = Cross-linked polyurethane.

ii = Linear thermoplastic polyurethane.

iii = Cross-linked epoxy.

iv = Cross-linked poly(methacrylate).

v = Linear thermoplastic poly(methacrylate).

** A = PTMO 2000.

Table 11. Descriptions of Three-Component IPNs.

IPN Abbreviation	IPN Type*	Composition (% by Wt.) Polyurethane-Epoxy-Acrylic	Charge Group Concentration Percent		
			Polyurethane	Epoxy	Acrylic
CP/0510/BMA	I	80-10-10	—	0.54	—
NPU/0510/DMA	II	80-10-10	0.38	0.54	0.89
(BrPU/0510/DMA) ₁	III	90-05-05	2.66	0.27	0.45
(BrPU/0510/DMA) ₂	III	80-10-10	2.37	0.54	0.89
(BrPU/0510/DMA) ₃	III	70-15-15	2.07	0.81	1.34
(BrPU/0510/DMA) ₄	III	60-20-20	1.78	1.08	1.78
(BrPU/0510/DMA) ₅	III	50-25-25	1.48	1.35	2.23
LBrPU/0510/DMA	IV	80-10-10	2.37	0.54	0.89
BrPU/0510/LDMA	IV	80-10-10	2.37	0.54	0.89
LBrPU/0510/LDMA	IV	80-10-10	2.37	0.54	0.89
BrPU/0510/IEM	V	80-10-10	2.37	0.54	—

* Type-I = IPN without charge groups.
 Type-II = IPN with similar charge groups.
 Type-III = IPN with opposite charge groups.
 Type-IV = Pseudo-IPN (P-IPN).
 Type-V = Graft-IPN (G-IPN).

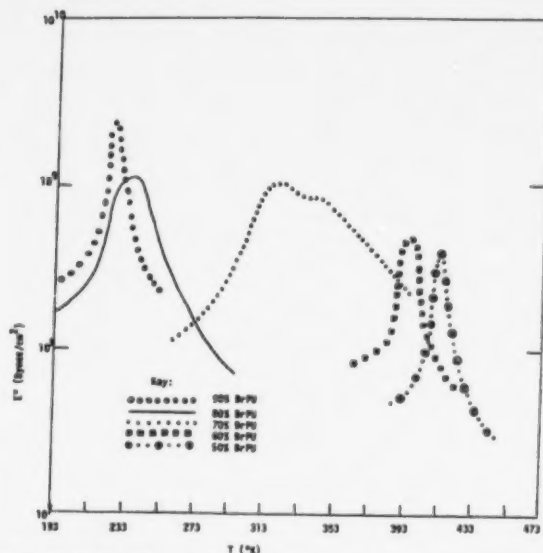


Fig. 1. Effect of varied composition in Type-III IPNs (opposite charge) on mechanical spectra.

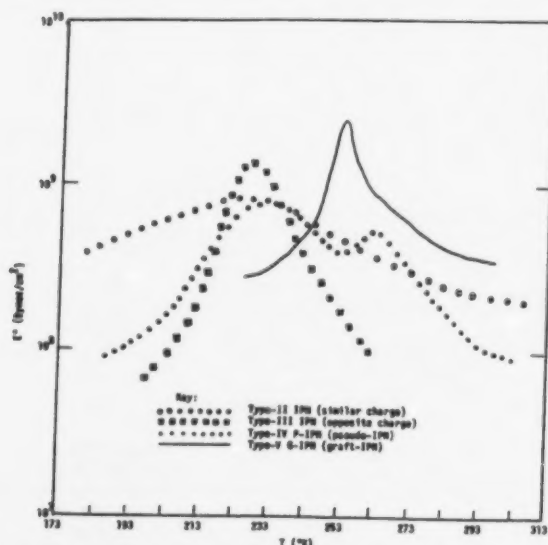


Fig. 2. Comparison of the mechanical spectra for four types of polymer alloys.

Table 12a. Glass Transition Temperatures (T_g s) of Polyurethane, Epoxy, and Acrylic Homopolymers by Rheovibron.

Sample*	T_g (K)
CU	207
NPU	219
BrPU	216
LBrPU	211
0510	447
BMA	313
DMA	322
LDMA	320

* See Table 10 for descriptions of samples.

Table 12b. Glass Transition Temperatures (T_g s) of Three Component IPNs by Rheovibron.

IPN**	T_g (K)
CU/0510/BMA	226
NPU/0510/DMA	224
(BrPU/0510/DMA) ₁	223
(BrPU/0510/DMA) ₂	228
(BrPU/0510/DMA) ₃	316
(BrPU/0510/DMA) ₄	394
(BrPU/0510/DMA) ₅	415
LBrPU/0510/DMA	222
BrPU/0510/LDMA	229
LBrPU/0510/LDMA	231, 264
BrPU/0510/IEM	254

** See Table 11 for descriptions of IPNs.

Table 13. Mechanical Properties of Polyurethane, Epoxy, and Acrylic Homopolymers.

Sample	M_{100} MPa	M_{200} MPa	TS MPa	E (%)	H (Shore A)	H (Shore D)
CU	7.2	12.8	20.7	568	67	17
NPU	9.3	13.7	22.0	777	68	18
BrPU	8.9	13.4	21.3	555	75	24
LBrPU	7.9	11.9	20.6	586	73	21
0510	—	—	59.4	2	97	84
BMA	—	—	33.4	15	91	59
DMA	—	—	30.4	13	90	56
LDMA	—	—	28.9	14	89	54

components, which increased the chance for interpenetration of the networks. The Type-IV PDIPN (pseudo-IPN) prepared from crosslinked polyurethane and epoxy with linear thermoplastic acrylic

Table 14. Mechanical Properties of Three Component IPNs.

IPN	M ₁₀₀ MPa	M ₂₀₀ MPa	TS MPa	E (%)	H (Shore A)	H (Shore D)
CU/0510/BMA	17.0	—	30.7	185	78	28
NPU/0510/DMA	27.0	—	31.9	128	80	30
(BrPU/0510/DMA) ₁	9.9	23.8	25.0	325	76	25
(BrPU/0510/DMA) ₂	24.6	—	32.4	145	87	35
(BrPU/0510/DMA) ₃	—	—	33.6	75	94	40
(BrPU/0510/DMA) ₄	—	—	34.8	26	97	58
(BrPU/0510/DMA) ₅	—	—	35.7	15	98	67
LBrPU/0510/DMA	24.1	—	27.2	175	88	36
BrPU/0510/LDMA	25.9	—	31.0	142	84	39
LBrPU/0510/LDMA	20.8	—	25.6	191	79	30
BrPU/0510/IEM	26.7	—	33.1	132	80	3

(BrPU/0510/LDMA) exhibited better properties than the other two PDIPNs. In this case only the acrylic polymer (10 percent by weight) was linear, so it was still possible for the BrPU and epoxy networks to interpenetrate with one another. The lowest mechanical properties were exhibited by the PDIPN containing both linear polyurethane and acrylic polymers (LBrPU/0510/LDMA) due to the absence of a permanent interpenetration of networks. By increasing the concentrations of epoxy and acrylic polymers, a higher tensile strength, modulus and hardness, as well as decreased elongation were observed for the Type-III IPNs. This was due to an increased rigid structure in the IPNs and a higher crosslink density.

A comparison of experimental and calculated ultimate tensile strengths for the three-component IPNs is shown in Table 15. The calculated tensile strengths were obtained from the linear additivity of the constituent homopolymer tensile strengths based upon weight fraction. In all of the three-component IPN types, ΔT_s were positive, which indicates that the IPNs exhibited mechanical properties that were improved over a mere blending of the constituent polymers. For IPNs of the same composition (PU/PE/PA = 80/10/10) the percent difference was highest for the Type-III IPN (opposite charge) (25 percent) and lowest for the PDIPN containing the linear polyurethane and acrylic polymers (1 percent). Obviously, the high degree of interpenetration and good compatibility in the former case led to an experimental tensile strength which was much higher than that calculated.

CONCLUSIONS

To summarize, two and three component IPNs have been prepared from polyurethanes, epoxies,

Table 15. Comparison of Experimental and Calculated Ultimate Tensile Strengths of Three Component IPNs.

IPN	TS		ΔT_s MPa	Percent Difference
	Experimental MPa	Calculated MPa		
CU/0410/BMA	30.7	25.9	4.8	19
NPU/0510/DMA	31.9	26.6	5.3	20
(BrPU/0510/DMA) ₁	25.0	23.6	1.4	6
(BrPU/0510/DMA) ₂	32.4	26.0	6.4	25
(BrPU/0510/DMA) ₃	33.6	28.4	5.2	19
(BrPU/0510/DMA) ₄	34.8	30.7	4.1	13
(BrPU/0510/DMA) ₅	35.7	33.1	2.6	8
LBrPU/0510/DMA	27.2	25.4	1.8	7
BrPU/0510/LDMA	31.0	25.9	5.1	20
LBrPU/0510/LDMA	25.6	25.3	0.3	1

and acrylics. It is apparent that increasing homogeneity of these IPNs results in enhanced mechanical properties. Factors which result in these effects include presence of charge groups in both polymers (opposite charges yielding the most significant effects), decrease in molecular weight of the prepolymer precursors to the IPNs, and intentional grafts between the component networks.

Since all the above systems may readily be processed by reactive techniques (e.g. reaction injection molding), it is apparent that these materials may be candidates for uses in areas where thermosetting materials with selected mechanical properties are desired.

REFERENCES

1. A comprehensive monograph in this field is Yu. Lipatov and L. Sergeeva, "Vzaimopronikayushchie setki," (Interpenetrating Polymer Networks), Naukova Dumka, Kiev (1979) (in Russian).
2. Early citations to one-component IPNs are J. R. Millar, *J. Chem. Soc.* 1311 (1960); K. Shigayama and Y. Suzuki, *Kobunshi Kagaku*, 23, (249), 24, (1966); K. Shibayama, *Zairyo*, 12, 362 (1962); K. Shigayama, *Kobunshi Kagaku*, 19, 219 (1962), *ibid.*, 20, 221 (1963).
3. H. L. Frisch, D. Klempner, and K. C. Frisch, *J. Polym. Sci., Polym. Letters*, 7, 775 (1969); H. L. Frisch, D. Klempner, and K. C. Frisch, *J. Polym. Sci. A-2*, 8, 921 (1970); M. Matsuo, T. K. Kwei, D. Klempner, and H. L. Frisch, *Polym. Eng. Sci.*, 10, 327 (1970); D. Klempner and H. L. Frisch, *J. Polym. Sci., (B)* 8, 525 (1970).
4. L. H. Sperling and D. W. Friedman, *J. Polym. Sci., A-2*, 7, 425 (1969); L. H. Sperling, D. W. Taylor, M. L. Kirkpatrick, H. F. George, and D. R. Bardman, *J. Appl. Polym. Sci.*, 14, 73 (1970); L. H. Sperling, H. F. George, V. Huelck, and D. A. Thomas, *J. Appl. Polym. Sci.*, 14, 2815 (1970).
5. H. L. Frisch and D. Klempner, *Adv. Macromol. Chem.* 2, 149 (1970).
6. D. Klempner, *Angew. Chem.*, 17, 97 (1978).
7. D. J. David, "Analytical Chemistry of Polyurethanes," Vol. XVI, Wiley-Interscience, New York, 138 (1969).

Morphological Studies of Oriented Ultra-High Molecular Weight Polyethylene with Enhanced Planar Mechanical Properties

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Ultra-high molecular weight polyethylene films prepared by melt flow crystallization under torsional flow conditions were characterized by wide angle (WAXS) and small angle (SAXS) diffraction techniques and scanning electron microscopy (SEM). The films had a fibrillar morphology in which lamellae having an average fold period of 650Å were stacked with their c-axis along the circular flow lines. X-ray analysis showed that the a- and b-axes were preferentially oriented along the thickness and radial directions of the sample.

INTRODUCTION

Many studies have been made on the development of polymers with high degrees of chain orientation and extension. This stage of high anisotropy has been achieved with semi-crystalline and liquid crystalline polymers using solid state deformation and melt or solution flowing processes in which the polymer is deformed typically under uniaxial flow conditions (1 to 3). As a result, the fibrillar products from these processes have a high level of molecular orientation in one direction only and consequently their resultant mechanical properties are very directional. A recent report (4, 5) discussed a new process for the development of fibrillar morphologies with high modulus and strength in planar directions using curvilinear flow conditions. The approach was unique because it allowed the preparation of fibrillar morphology in which the orientation of the fibrils had an angle gradient on both the plane and the thickness direction of the sample. Similar studies were performed also with ultra-high molecular weight polyethylene using the simple torsional flow field of a circular plate-plate rheometer (6). The polymer was oriented in the optical apparatus by melt flow crystallization and resulted in multiaxially oriented and birefringent fibers with high modulus along and across the flow lines. In this report, we discuss some

results on the morphology and crystalline structure of the so produced multiaxially oriented UHMWPE films which were obtained by x-ray diffraction techniques and electron microscopy.

METHODS AND MATERIALS

The oriented ultra-high molecular weight polyethylene (UHMWPE HiFax 1900 $M_w \geq 2 \times 10^6$) was prepared in the optical rheometer described in detail elsewhere (6). The plate-plate system of the rheometer was designed so that the polymer could be sheared under modest compression. The processing condition for the preparation of the oriented UHMWPE morphologies were decided by the results of previous studies with UHMWPE melts (6). The polymer melt was heated to 320°C and after thermal equilibration for 5 minutes it was compressed gently and sheared by rotating the lower plate at a shear rate $\sim 2.4 \times 10^2 \text{ sec}^{-1}$. Oriented films (60 to 100 μm thick) were obtained by flow crystallization, which occurred as the melt was cooled to ~ 100 to 110°C. When the polymer solidified completely, the rotation was stopped and the oriented film was retrieved after cooling to ambient temperature.

Samples for the x-ray diffraction studies were cut from the disc-shaped UHMWPE oriented films as shown in Fig. 1. Wide-angle (WAXS) and small-

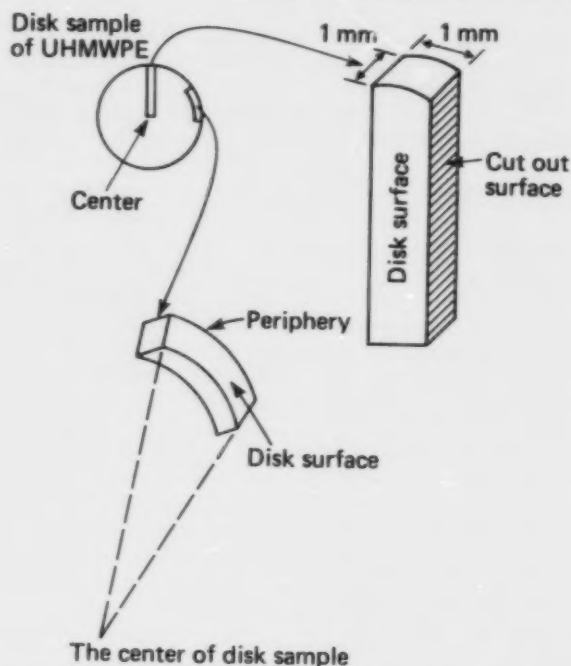


Fig. 1. Schematic drawing of the position of the cut out samples from the multiaxially oriented UHMWPE films for x-ray analysis.

angle (SAXS) x-ray diffraction photographs of the samples were obtained with a flat plate and small-angle vacuum camera, respectively, using Ni-filtered Cu-K α radiation generated at 40 kV and 39 mA on a Rigaku RD-3A diffractometer. For the measurements of SAXS, the incident beam was collimated with two collimators having a pinhole diameter of 0.5 mm (the first) and 0.3 mm (the second), which were placed 40 cm apart. The sample to x-ray film distance was 43 cm, which was the limit to achieve a suitable contrast of the SAXS patterns under the present conditions. The surface morphology of the oriented films was studied by scanning electron microscopy using a Hitachi S-500 SEM microscope. The samples were coated with carbon for stability.

RESULTS AND DISCUSSION

The melt flow crystallization of UHMWPE under simple torsional flow conditions was discussed in some detail in a recent report (6). Under the torsional flow conditions of our studies, the polymer melt crystallized by row nucleation along the circular flow lines into a fibrillar morphology. Scanning electron microscopy indicates that the fibrils were lamellar with the lamellae perpendicular to the flow direction and with an average thickness of $\sim 500\text{\AA}$ (Fig. 2). However, more information about the crystalline structure of the fibrillar morphology was obtained by the x-ray diffraction studies. Figure 3 shows the WAXS and SAXS diffraction patterns recorded with the incident x-ray beam along (a) the circumferential, (b) the radial, and (c) the normal or thickness direction of the disc-sample. Figure 3(a) was recorded with the incident beam parallel

to the radial direction of the sample, which is the two-direction in Fig. 4, and with the circumferential direction of the sample in a vertical position relative to the photograph mounting. Figure 3(b) was recorded with the incident beam parallel to the normal or thickness direction of the specimen, which is the three-direction in Fig. 4, and with the circumferential direction of the sample also in the vertical position. Figure 3(c) was recorded with the incident beam nearly parallel to the circumferential direction, i.e., the one-direction in Fig. 4, and with the radial direction of the sample in the vertical posi-

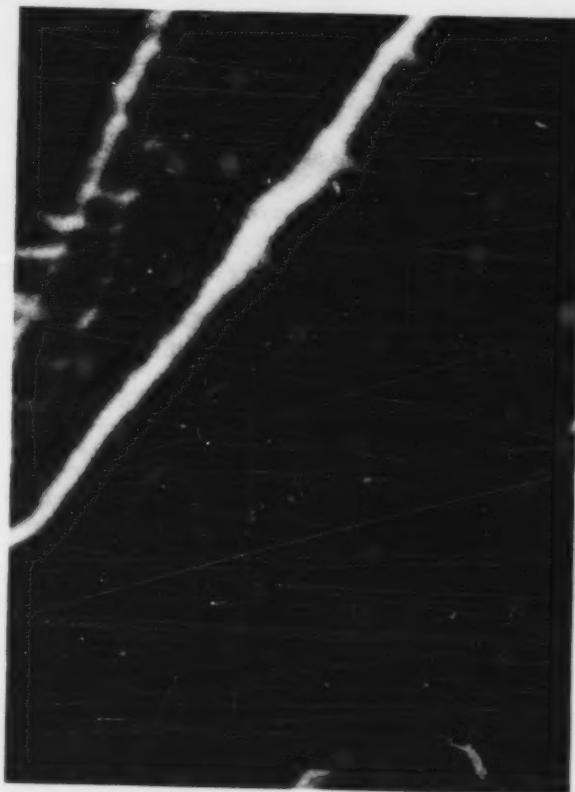


Fig. 2. Scanning electron micrograph of the surface morphology of a fibrillar UHMWPE obtained by melt flow crystallization under the combined effects of compression and torsional flow.

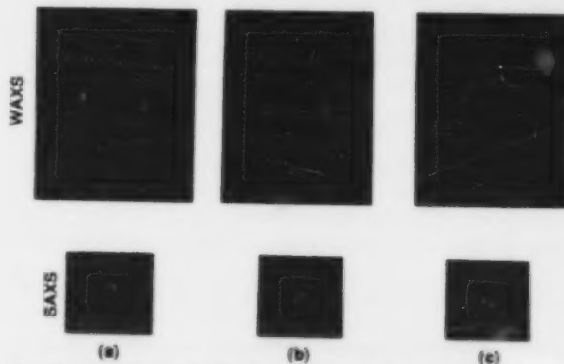


Fig. 3. WAXS and SAXS photographs of the melt crystallized UHMWPE morphologies under the combined effects of compression and torsional flow.

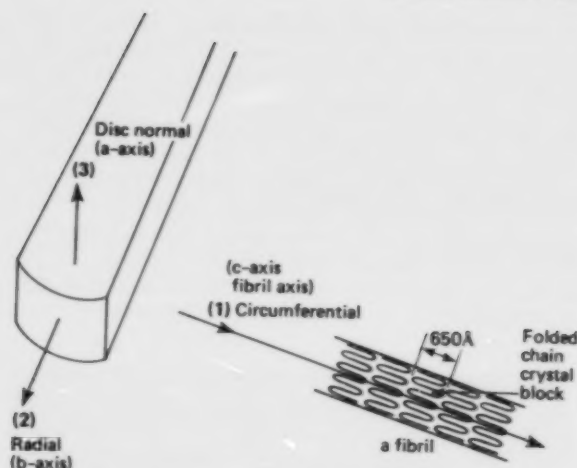


Fig. 4. Schematic drawings of the relative orientations of the unit cell axes *a*, *b*, and *c* and the folded chain crystal blocks within a fibril.

tion. When an x-ray photograph was taken with incident beam parallel to the radial direction, the intensity of the (200) reflection increased and was comparable to that of the (110) reflection, as shown in Fig. 3(a). As the circumferential direction of the disc sample corresponds to the vertical in the present mounting of the photograph, it is apparent that the *a*-axis orients preferentially along the normal to the disc sample surface. When the incident beam was directed parallel to the disc normal, the (020) reflection was intensified as seen on the WAXS pattern in Fig. 3(b), indicating that the *b*-axis orients preferentially along the radial direction of the disc. The preferential orientation of the *a*- and *b*-axis is not clear in Fig. 3(c), probably due to the poor nature of the photograph caused by the characteristic gradient of chain orientation along the circumferential direction which inevitably deviates slightly from the incident x-ray direction. All the

WAXS patterns clearly show that the *c*-axis is fairly well oriented along the circumferential and hence shear direction.

The long period estimated from the SAXS maxima is $600 \pm 100\text{\AA}$. This large value implies that the melt flow crystallization occurred at a low degree of supercooling and hence at a high temperature. This is in agreement with the rheo-optical observations of fibrous crystal growth at $\sim 140^\circ\text{C}$ under torsional flow conditions, and is presumably due to the combined effects of the applied pressure and shear which might induce amorphous chain orientation along the shear direction. The SAXS patterns in Figs. 3(a) and (b) are extended, respectively, along the normal and radial direction of the disc sample whereas the SAXS pattern in Fig. 3(c), which was obtained with the incident beam along the circumferential direction, shows only strong void scatterings. These data indicate that the multiaxially oriented UHMWPE sample has basically a fibrillar morphology in which the chain folded crystal blocks, with an average fold period of $\sim 650\text{\AA}$, are stacked along the fibrils; the fibrils are oriented along the circumferential and hence along the applied shear direction. A schematic of the orientation of the unit cell axes, microfibrils, and the chain folded crystal blocks within a microfibril is shown in Fig. 4.

REFERENCES

1. *The Strength and Stiffness of Polymers*, edited by A. E. Zachariades and R. S. Porter, Marcel Dekker, Inc., New York, (1983).
2. T. Kanamoto, A. Tsuruta, K. Tanaka, M. Takeda, and R. S. Porter, *Polymer J.*, **15** (1983).
3. *Ultra-High Modulus Polymers*, edited by A. Ciferri and I. M. Ward (Applied Science Publishers Co., Barking, Essex, England, 1979).
4. A. E. Zachariades and J. Economy, *Polym. Eng. Sci.* **23**, 266 (1983).
5. A. E. Zachariades, *J. Appl. Polym. Sci.*, **29**, 867 (1984).
6. A. E. Zachariades and J. A. Logan, *J. Appl. Polym. Sci.*, **28**, 1837 (1983).

Processing of Reinforced Plastics Using Multi-Screw Compounders

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Polymer modification by addition of reinforcing agents represents a popular means of increasing physical property values. The polymer matrix has been forced to accept up to 55 percent by weight of fibrous reinforcement and 80 percent by weight of powdered types in order to meet application requirements. These materials demand sophisticated mixing equipment which must provide extensive intake and conveying capabilities, polymer wetting of reinforcement, and dispersion of reinforcement. This process must also be conducted with controlled shear intensity and excellent temperature and residence time control in order to respect polymer thermal sensitivity and product requirements. The extrusion process is a proven economical method for incorporating reinforcements into polymer resins. Co-rotating intermeshing twin-screw extruders are particularly suited for these tasks. Positive conveying, self-wiping, and shear intensive mixing characteristics provided by the screw mechanism satisfy requirements of reinforcement compounding. This mechanism allows interruption of streamline flow which is needed to disperse both high and low aspect ratio reinforcing agents into a polymer matrix. Mathematical representation of the benefits of twin-screw extrusion (relative to single-screw) related to pumping and mixing capability have been developed based on the classical pressure flow continuity equation with proper selection of boundary conditions.

INTRODUCTION

Many polymers today are modified by the addition of reinforcing agents to strengthen the finished product. Fiberglass reinforcements can be used up to 55 percent of the total weight of the final material; other fillers can be used as high as 80 percent. Uniform distribution in the polymer matrix is necessary to maintain product quality.

Reinforcements are most effective at their optimum concentrations. An insufficient amount can result in premature failure; however, an increase in the amount of glass or carbon fiber will not produce a proportionate increase in performance. Sometimes the optimum level cannot be reached because of compounding equipment limitations such as intake characteristics, wetting fiber length, dispersion, and interfacial voids. Therefore, all critical criteria for the mixing operation must be evaluated when selecting compounding equipment.

In addition to the classic reinforcements such as mica, talc, glass, and carbon fibers, new materials are being tested as reinforcements. One of the new reinforcement developments arousing interest is the use of calcium sulfate because of its ability to

produce an anhydrous product for thermoplastics and a hemihydrate for thermosets. An unusual reinforcement being tested is ground-up printed-circuit board scrap, which consists of 50-50 glass and cured epoxy resins. Silicon carbide fibers are also being tested and have shown excellent strength properties and chemical resistance (1).

No matter how great the properties, the reinforcer must be adequately dispersed in the polymer to have its greatest effect. The availability of improved processing equipment has had a major influence on the type and levels of reinforcements used today.

The equipment for dispersing reinforcements into a polymer system must be capable of performing the following process tasks:

- Generating high shear for melting the polymer,
- Providing optimum shear during reinforcement dispersion, and
- Incorporation of reinforcer without exceeding degradation temperatures.

Good control over residence time distribution is an essential feature of a continuous system. The residence time distribution must be short and uniform to minimize heat history.

PREDICTING MIXING PERFORMANCE

When evaluating different systems for the incorporation of reinforcer, the technique for determining the suitability of equipment involves calculating the flow streamlines of the channel cross section and evaluating the flow according to these criteria (2):

- Perpendicular surface orientation of discrete phase to streamline,
- Streamline pass through the region of maximum shear, and
- Long total length of the streamline.

Screw extruders are laminar mixing devices, and, in modified form, they can be used for manufacturing reinforced plastics. The most common types of extruders are single-screw, co-rotating twin-screw, and counter-rotating twin-screw. An analysis of isothermal flow for incompressible Newtonian fluids through shallow channels of extruders with simple geometry is not an exact representation of polymer behavior in complex compounding equipment. However, these representations successfully predict mixing performance for simple geometries.

The solution of velocity profiles from screw equipment usually involves resolution of the equation of motion into down and cross-channel directions. Assuming constant material viscosity, the z direction continuity equation is

$$\frac{\partial P}{\partial z} = \mu \left(\frac{\partial^2 v_z}{\partial x^2} + \frac{\partial^2 v_z}{\partial y^2} \right) \quad (1)$$

Boundary conditions are selected in such a way that neither the physical significance of the extrusion principle, nor the geometry of the extrusion equipment is greatly distorted. For single-screw equipment, the solution is fairly simple. Establishing a rectangular coordinate system at the screw root and developing the channel and barrel in a plane surface allows an analysis whereby the material is dragged by the high velocity of the barrel surface. This is, in fact, the extrusion principle.

When the same coordinate system is applied to multi-screw equipment, some imagination should be used to visualize a flexible barrel, and the intermesh flow behavior must be treated separately. An alternate frame of reference for multi-screw equipment is the inner barrel surface, moving along axially with the screw. This more correctly represents the extruder geometry.

COMPARISON OF SINGLE AND CO-ROTATING TWIN-SCREW EXTRUDERS

For both machines, the screw geometry is developed into a plane (Figs. 1 and 2) and the frame of reference is placed on the screw root. Neglecting the influence of channel sides and assuming total fill, the down channel velocity distribution solves to

$$v_z = \frac{\pi D n}{\cos \phi} \frac{y}{h} + \frac{y^2 - hy}{2\mu} \left(\frac{\partial P}{\partial z} \right) \quad (2)$$

and by analogy, the cross-channel velocity solves to

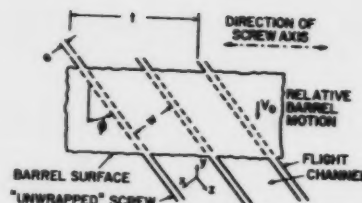


Fig. 1. Flat-plate model of a two-flight single-screw extruder.

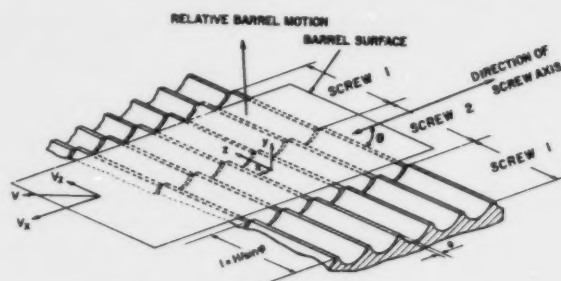


Fig. 2. Theoretical model for screw elements.

$$v_x = \frac{\pi D n}{\sin \phi} \frac{y}{h} + \frac{y^2 - hy}{2\mu} \left(\frac{\partial P}{\partial x} \right) \quad (3)$$

The flow analysis is identical for single- and twin-screw extruders where the crest width, e , is zero. This is because the total volume of material is forced to transport between screws in twin-screw, co-rotating, and fully intermeshing extruders at each intermesh.

Neglecting leak flows, the net velocity of cross-channel flow is zero, which implies circulatory flow. The flow streamline is helical in the screw channel; higher die pressure increases circulation in the cross-channel plane and, correspondingly, total shear and residence time.

Although the additional work due to circulatory flow contributes to phase distribution, the phases soon align on streamline and deform to slender bodies without breaking up. A change in the streamline direction is required to reorientate the disperse phase more favorably to the shear direction. In single-screw extruders, this is achieved with mixing pins or special shear sections. In co-rotating twin-screws, it occurs in the intermesh area and through the use of kneading blocks.

Because of significant screw crest widths, e , in twin-screw intermeshing co-rotating extruders, a twist restraint is imposed upon the material at intermesh (Fig. 3). The restraint causes an intermesh velocity term, $v_a = 2ne$, to be superimposed upon the v_z velocity term. This results in intermittent increases in the circulating channel velocity. The ability of an extruder to generate high pressure gradients can be useful in creating high circulatory flow several times in the extrusion operation. High sustained strain fields have limitations in dispersion because of unfavorable phase alignment. They can also cause overheating by viscous dissipation.

Machinery capable of developing high pressure gradients would be capable of imposing high strain

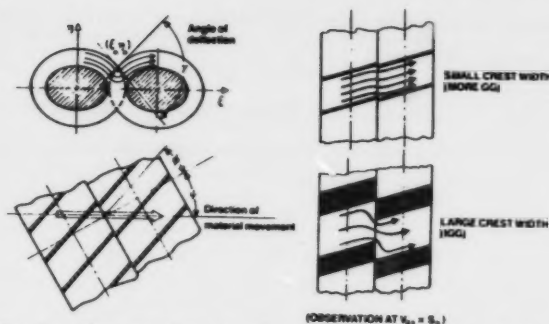


Fig. 3a. Change of flow direction of the wedge volume (absolute movement).

Fig. 3b. Change in direction of material flow as a function of screw crests.

over a short interval. Throughput characteristics for single-screw and twin-screw extruders have been described by Squires and Booy (3, 4). Total throughput is the difference between drag and pressure flow.

$$Q = Q_D - Q_P \quad (4)$$

The drag and pressure flows are simply represented by the integral of velocity profile and corrected by shape factors associated with drag and pressure flows in the presence of channel walls.

$$Q_D = \frac{1}{2} n F_D \frac{\pi D n}{\cos \phi} w h \quad (5)$$

$$Q_P = n F_P \frac{h^3 w}{12 \mu} \frac{\partial P}{\partial z} \quad (6)$$

$$\frac{\partial P}{\partial z} = \frac{Q_D - Q}{f_P n (h^3 w / 12 \mu)} \quad (7)$$

Figure 4 shows that the drag and pressure shape factors are much different for the two machines. Specifically, the difference between drag and pressure flow shape factors is larger for the twin-screw, co-rotating extruder than the corresponding single-screw extruder. Thus, twin-screw extruders can build pressure in shorter length than a corresponding single screw.

FLEXIBILITY

An important feature of the existing co-rotating, intermeshing twin-screw extruders is the ability to modify the extruder to meet changing process demands (Fig. 5). The screw section can be made up from a wide selection of different types of kneading blocks and screw elements that slide onto keyed shafts. Each individual screw element provides a distinct conveying, shear, or pressure buildup action which can be controlled. As a result, processing conditions at different locations along the screws can be varied so that a high shear or intensive mixing action can be obtained at one location, and increased pressure generated at another section. The ability to vary and accurately control conditions anywhere along the process length is an important advantage of the ZSK system.

Individual barrel sections are assembled together

to obtain the desired process length. The different barrel designs are available to allow multiple feeding of ingredients, injection of liquids and solids, and venting of moisture or removal of volatiles anywhere along the process section.

For several good reasons, co-rotating, intermeshing, twin-screw compounding extruders have become more and more important for glass fiber composite production. Variability of screw design is particularly important for producing glass fiber reinforced composites, since it is possible to vary the required average glass fiber length distribution, depending on the polymer and percentage of glass used. Polymers with high melt viscosities or high glass loadings (55 percent by weight or more) require milder screw configuration than polymers of low melt viscosity or low percentage glass fiber (30 percent by weight or less).

Narrow kneading disc elements or screw elements with reversed flights can be used to determine the final fiber length distribution as well as the physical properties. The effect of a screw configuration on physical properties is shown in Table 1. The properties are relative, and no specially treated polypropylene was used.

A convenient method for determining the proper screw configuration for optimum results is to ash the compound and then count the magnified fiber images using a graphics table connected to an image analyzer (5). By evaluating the results of tests for different screw configurations, the formulator can choose the screw that gives the optimum results.

The incorporation of reinforcements into a polymer requires three distinct sequences. In the first step, the polymer must be melted. This is accom-

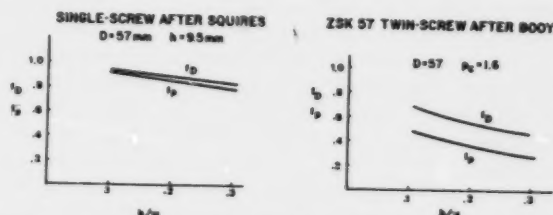


Fig. 4. Drag and pressure shape factors calculated according to Squires (3) and Booy (4).

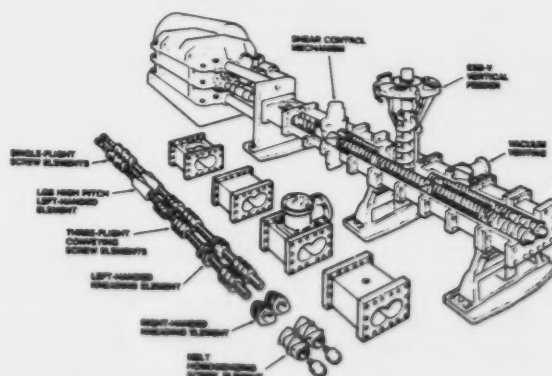


Fig. 5. ZSK twin-screw, co-rotating, self-wiping extruder.

Table 1. Effect of Compounding on Mechanical Properties of Fiber Glass-Filled Polypropylene.

	Compounding Technique					
	Single-Screw Extruder	Continuous Mixer	Twin-Screw Compounder 1	Twin-Screw Compounder 2	Twin-Screw Compounder 3	Twin-Screw Compounder 4
Wt. % glass fiber	25	25	25	23	25	25
Type of fibers	1/4" Chopped glass	1/4" Chopped glass	Roving	Roving	Roving	1/4" Chopped glass
Tensile strength psi	6100	4700	4900	5800	8000	8000
Flex. modulus M psi	580	460	600	550	550	550
Izod impact ft. lb/in. notched	1.45	0.7	0.9	1.1	1.2	1.3
Heat defl. temp. C 264 psi °F	264	153	203	184	268	266
% of fibers smaller than .5 mm	—	—	—	—	29	—
Remarks		Glass was fed into the feed section	Screw with very strong sections after addition of glass	Moderate screw after addition of glass	Mild screw after addition of glass (No. 14)	

plished by applying the proper shear and heat in order to avoid degradation. Additives such as flame retardants, pigments and plasticizers can be compounded in this section.

In the second stage of the process, the fibers must be added to the melt and thoroughly mixed. The glass can be added in chopped form or introduced into the melt as rovings through an open degassing adaptor without special metering (Fig. 6). The strands are unwound continuously from the cores and pulled into the machine by the rotating screws. The amount of glass is controlled by the number of strands and the speed of the screws. The polymer feed rate can be readily varied because twin-screw extruders are generally starve-fed with no adjustment required in screw speed.

Chopped glass can also be fed downstream into the molten polymer, but metering equipment is required. The glass can be fed by gravity through an LS (open) barrel (Fig. 7). With chopped glass, fiber has only to be wetted by polymer, the volatiles removed, and the compound discharged through a die. For most polymers, a small, neutral kneading section or a reverse screw element is included. Downstream feeding can also be used for other reinforcing or nonreinforcing fillers, particularly if they are abrasive.

In the third step, pressure must be generated to force the reinforced plastic through a die to be pelletized. This allows ease of handling for further processing of finished products.

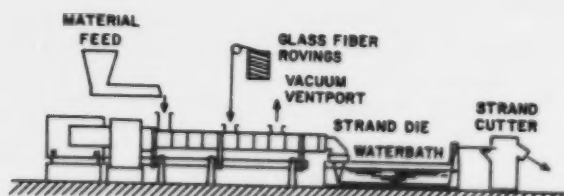


Fig. 6. Typical arrangement for feeding continuous glass fiber rovings.

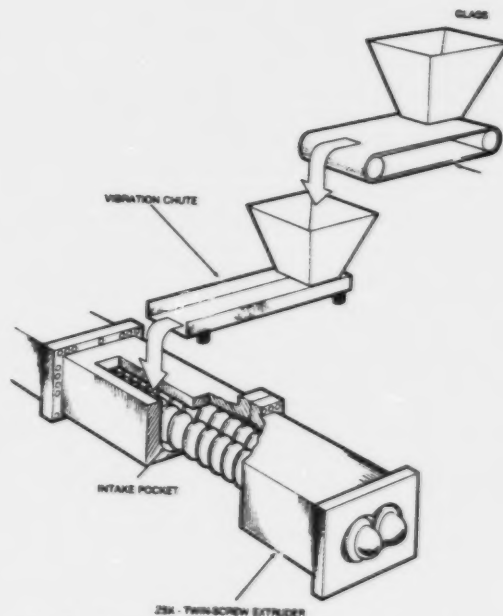


Fig. 7. Downstream feeding via "LS" type barrel.

REFERENCES

1. M. Colangelo and M. H. Naitove, *Plastics Technol.*, **29**, 103 (1983).
2. S. Irving, Ch. 8 of "Polymer Mixing Technology," V. H. Uhl and J. B. Gray, Eds. Vol. 2, Academic Press, New York, N. Y., (1967).
3. P. H. Squires, Ch. 4, of "Processing of Thermoplastics Materials," E. C. Bernhardt, Ed., Reinhold (1959).
4. M. L. Booy, *Polym. Eng. Sci.*, **20**, 1220 (1980); H. Werner and K. Eise, 37th SPE ANTEC, *Tech. Papers*, **25**, 181 (1979).
5. P. R. Hornsby, *Plastics Compound.*, **6**, 65 (1983).

NOMENCLATURE

- P —Coordinate directed pressure.
 μ —Newtonian viscosity.
 v —Local velocity.
 $x y z$ —Coordinate.

Processing of Reinforced Plastics Using Multi-Screw Compounders

D	—Screw diameter.	f_D	—Channel shape factor for drag flow.
n	—Screw RPM.	f_P	—Channel shape factor for pressure flow.
h	—Screw channel depth.	w	—Channel width.
ϕ	—Helix angle measured from machine cross section.	Q_R	—Recirculating flow in kneading blocks.
e	—Screw crest width.	ρ_C	—Centerline distance ratio for co-rotating, intermeshing twin screws.
v_a	—Local axial velocity term.	C_L	—Centerline distance.
Q	—Volumetric throughput.	R	—Screw radius.
Q_D	—Drag flow, volumetric throughput of screw in absence of head pressure.	ϵ	—Degree of fill.
Q_P	—Pressure flow, less volumetric throughput due to head pressure.	ξ_0	—Coordinate.
		η_0	
		S_n	—Crest width.

Impact Energy Absorption of Unidirectional Glass Fiber-Epoxy Composites

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The influence of resin and fiber properties on the impact behavior of composites can be assessed in a three-point drop-weight impact test by varying the length-to-thickness ratio of the specimen. The fracture initiation energy per unit deformed volume, w_i , can be described by the expression:

$$w_i = \frac{\tau_{11}^2}{18E_{11}} + \frac{4\tau_{12}^2}{15G_{12}}$$

where τ_{11} is the tensile stress, τ_{12} is shear stress; E_{11} is tensile modulus; and G_{12} is shear modulus. A unidirectional glass fiber-epoxy composite was tested at impact velocities of 2.2 m/s (5 mph) and 4.5 m/s (10 mph). The energy to initiate fracture, w_i , was in the range of 2 to 3.5 MJ/m³, apparently independent of impact velocity. The total energy absorbed by the impacted composite was also found to be independent of impact rate but very sensitive to the length to thickness ratio: about 13 and 3.5 MJ/m³ at the corresponding ratios of 4.6 and 23. It was generally observed that high fracture energy is associated with extensive specimen delamination, i.e. failure in shear.

INTRODUCTION

The extremely fast instrumented systems for data acquisition and analysis available today provide a new wealth of information about material behavior during high speed impact testing. Strain gages, capable of measuring the load on the impacted specimen in time increments as low as 3 microseconds, are commonly used (1, 2). A laser-Doppler velocimetry technique can also be used (3). The impact behavior of composites has been studied in some detail, both with respect to methodology of testing and the interpretation of the influence of composite construction on the measured fracture energy (4 to 7). Most authors have used some variation of the Charpy drop-weight test (three-point bend) in which the impacted beam specimen is placed between two anvils. It is well known that the tensile and shear stresses are influenced by the ratio of the span between the anvils, ℓ , to specimen thickness, d . Varying ℓ/d between 7 and 70, Chambers and McGarry have shown that shear effects become increasingly important as ℓ/d decreases (8). Because of shear effects, the error in measuring the bend modulus of a unidirectional glass fiber composite at ℓ/d of 16, for example, was estimated to be 12 percent (9). To minimize shear effects many authors test specimens at $\ell/d \geq 16$. The failure is then essentially a tensile failure dominated by the fibers.

To study the influence of the resin as well, we have conducted a series of impact tests of a unidirectional glass-epoxy composite in which ℓ/d was varied between 3 and 24, thus allowing analysis of impact behavior in terms of both resin and fiber properties.

ANALYSIS

In a three-point bend the beam is subjected to normal and shear stresses. The highest tensile stress, τ_{11} , is at outer mid-span.

$$\tau_{11} = \frac{3F_i \ell}{2bd^2} \quad (1)$$

Where F_i is the load at the onset of fracture, applied at the beam center, ℓ is the span between the two end supports, b is the beam width, and d is the beam thickness. The highest shear stress, τ_{12} , is at the mid-plane of the beam.

$$\tau_{12} = \frac{3F_i}{4bd} \quad (2)$$

Both stresses contribute to the deflection of the beam, the relative contribution being dependent on the magnitude of each stress and, hence, on the ratio ℓ/d . The equation of beam deflection accounting for shear effects is (8):

$$\Delta_i = \frac{F_i(\ell/d)^3}{4bE_{11}} \left[1 + \frac{6}{5} \frac{E_{11}}{G_{12}} \left(\frac{d}{\ell} \right)^2 \right] \quad (3)$$

Where Δ_i is the deflection at fracture initiation and E_{11} and G_{12} are the tensile and shear moduli, respectively. Defining an apparent modulus, E_A , as

$$\Delta_i = \frac{F_i(\ell/d)^3}{4bE_A} \quad (4)$$

we obtain

$$\frac{1}{E_A} = \frac{1}{E_{11}} + \frac{6}{5G_{12}} \left(\frac{d}{\ell} \right)^2 \quad (5)$$

Assuming a linear elastic fracture, the work done to fracture the beam W_i , is

$$W_i = \frac{1}{2} F_i \Delta_i \quad (6)$$

Substituting Eqs. 1, 2, and 3 and rearranging yields

$$W_i = \frac{\tau_{11}^2}{18E_{11}} \ell bd + \frac{4\tau_{12}^2}{15G_{12}} \ell bd \quad (7)$$

Hence, the work per unit deformed volume, w_i , is

$$w_i = \frac{\tau_{11}^2}{18E_{11}} + \frac{4\tau_{12}^2}{15G_{12}} \quad (8)$$

Equation 8 describes the contribution of tension and shear to the fracture initiation energy of the beam.

In the automated instrumented impact testing, Δ_i and w_i can be calculated from the force-time data and the known values of the striking hammer mass and impact velocity (1, 2).

EXPERIMENTAL

Material

A unidirectional Scotchply (3M Company) with a nominal thickness of 0.64 cm (0.25 inch) was used. It is constructed of 17 plies with the second and sixteenth ply in 90° to the principal direction. The glass content was determined by pyrolysis to be 45.3 percent by volume and, hence, is 40 percent in the principal direction (15 of 17 plies). The specimens were cut to a nominal width of 0.953 cm and a length of 4 cm over the span length. Prior to testing the specimens were preconditioned for 1 hour at 170°C then placed in a desiccator.

Procedure

The drop-weight impact tests were conducted on a Dynatup Model 8200 with ETI-300 automated data acquisition and analysis system (Effects Technology, Inc., Santa Barbara, CA). The instrument striking tup and the anvils are designed according to ASTM E23 (Charpy test). A detailed description of the system is presented elsewhere (12). All specimens were tested in a three-point bend geometry with the principal fiber orientation aligned along the span. Notches were not used. The hammer and tup combined weight was 13.62 kg. Impact velocity

was changed by adjusting the drop height. Test temperature was 21°C.

An example of an impact test record is shown in Fig. 1. The load-time curve is linear up to a maximum load, taken to be the load required to initiate fracture. The successive receding loads are the record of the fracture propagation process. Fracture energies are computed by integration, as described by Ireland (2).

Impact testing at each span consisted of seven to ten specimens and the averages reported have standard deviation of about 5 percent for the load and about 10 percent for the fracture energy. A much wider scatter, which will be discussed later, was observed in the propagation energy at spans of 10 and 15 cm.

RESULTS

The impact data at 2.2 and 4.5 m/s are summarized in Tables 1 and 2. The span was varied between 2 and 15 cm corresponding to ℓ/d of 3.1 to 23.4. At a 2 cm span, toward the end of the impact event, the striking tup became tightly wedged between the two halves of the impacted specimens and, hence, it was not possible to obtain values of the propagation energy for that span.

Of the eight specimens tested at 2.2 m/s and 15 cm span only two fractured completely. The other six suffered damage to the outer fibers (highest normal stresses) while their core remained intact.

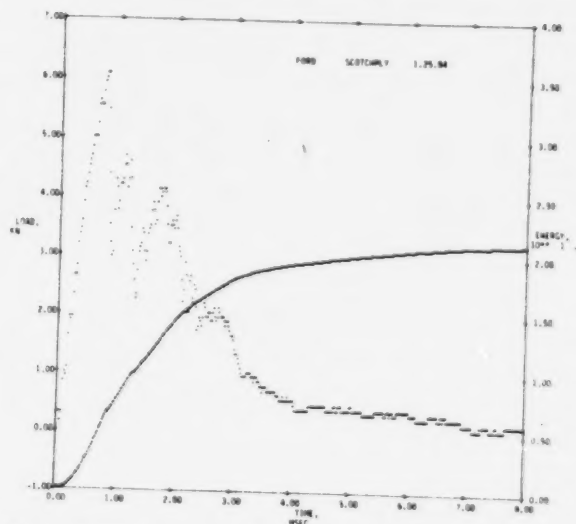


Fig. 1. Typical impact record of a unidirectional glass fiber composite.

Table 1. Summary of Impact Data of Unidirectional Scotchply, 0.64 cm Thick, at 2.2 m/s, 21°C.

Span $m \times 10^{-2}$	F_i N	t_i $s \times 10^{-3}$	ΔJ $m \times 10^{-3}$	τ_{11} MPa	τ_{12} MPa	W_i MJ/m ²	W_p MJ/m ²
2	6980	0.31	0.81	517	84	2.4	—
3	5926	0.67	1.40	674	72	2.7	9.7
4	5027	0.90	2.04	775	61	2.3	7.1
10	2700	6.4	12.9	1028	33	3.3	1.5
15	1906	15.2	29.0	1090	23	3.4	—

In fact, in these tests the striking hammer kept bouncing on the specimens till it came to rest. From the tests at 4.5 m/s, which resulted in complete failure of all the specimens, the fracture initiation energy was found to be 33 J. At 2.2 m/s the kinetic energy of the striking hammer was 34 J, apparently just enough to cause fracture initiation but not propagation in all the specimens.

Except for the tests at a span of 15 cm, the load-time record of the impacted specimens generally followed the one shown in Fig. 1. At the 15 cm span, large oscillations in the load were observed at fracture initiation (See Fig. 2). This occurred over a very short period and had a negligible effect, if any, on initial energy. But it made the maximum value of the load somewhat questionable. Yet, for lack of better values, we have used the maximum load for calculating τ_{11} and τ_{12} . Interestingly enough, the oscillations were more pronounced when the fractured specimens exhibited substantial fiber delamination as will be discussed later.

Plots according to Eq. 5 are shown in Fig. 3. Least squares analysis yields the expressions

$$2.2 \text{ m/s: } 1/E_A = 4.1 \times 10^{-11} + 0.95 \times 10^{-9} (\ell/d)^{-2}$$

$$4.5 \text{ m/s: } 1/E_A = 2.9 \times 10^{-11} + 1.1 \times 10^{-9} (\ell/d)^{-2}$$

from which one may calculate for 2.2 m/s: $E_{11} = 24$ GPa and $G_{12} = 1.3$ GPa; and for 4.5 m/s: $E_{11} = 34$ GPa and $G_{12} = 1.1$ GPa. Plots of τ_{11}^2/w_i versus τ_{12}^2/w_i

Table 2. Summary of Impact Data of Unidirectional Scotchply, 0.64 cm Thick, at 4.5 m/s, 21°C.

Span m $\times 10^{-2}$	F_i N	t_i s $\times 10^{-3}$	Δ_i m $\times 10^{-3}$	τ_{11} MPa	τ_{12} MPa	w_i MJ/m ²	w_p MJ/m ²
2	7070	0.15	0.80	535	87	2.1	—
3	6200	0.30	1.30	711	77	2.0	10.4
4	5256	0.44	2.10	804	64	2.0	6.0
6	4788	1.12	4.94	1068	58	3.3	2.0
8	3864	1.92	8.40	1188	48	3.4	0.7
10	3570	2.43	10.6	1312	43	3.3	0.3
15	2519	6.94	29.9	1446	30	3.5	1.7

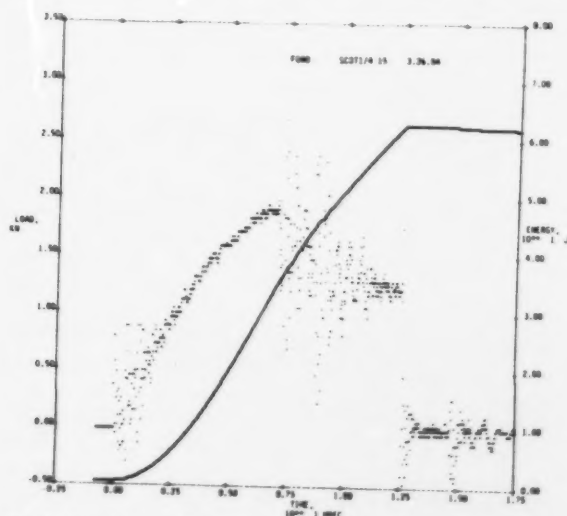


Fig. 2. Impact record at span of 15 cm showing load oscillation at fracture initiation.

with (Eq. 8) are shown in Fig. 4. When plotted in this way the intercept is $18E_{11}$ and the slope is $-24E_{11}/5G_{12}$. For 2.2 m/s, least squares analysis gives: intercept = 3.59×10^{11} Pa, slope = -84.1 and a correlation coefficient of 0.9735. From these we find that $E_{11} = 20$ GPa and $G_{12} = 1.1$ GPa. For 4.5 m/s the intercept is 5.54×10^{11} Pa, the slope is

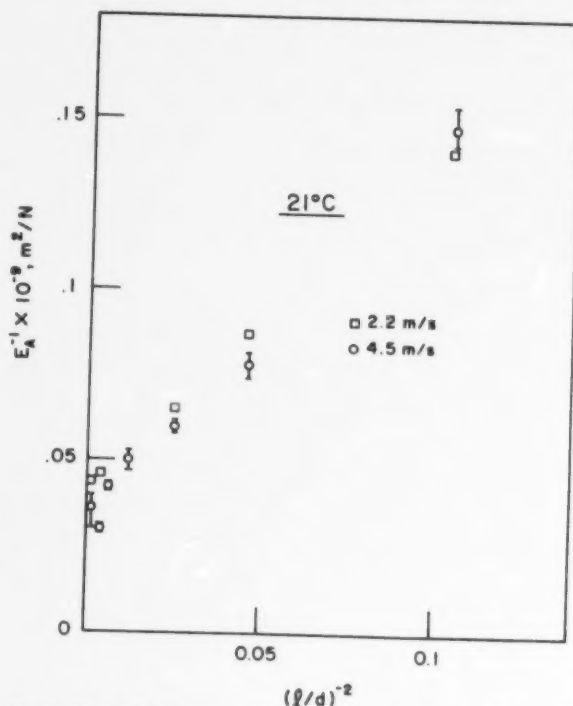


Fig. 3. Plots of E_A^{-1} versus $(\ell/d)^{-2}$ at impact velocity of 2.2 and 4.5 m/s.

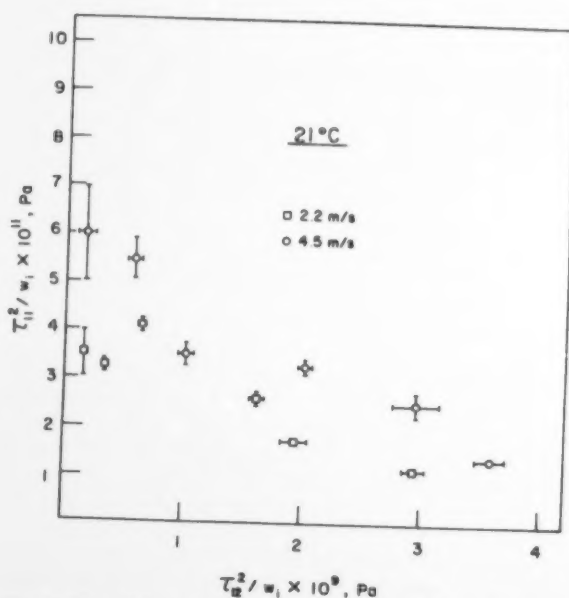


Fig. 4. Plots of τ_{11}^2/w_i versus τ_{12}^2/w_i at impact velocity of 2.2 and 4.5 m/s.

-114, and the correlation coefficient is 0.93. Hence, $E_{11} = 31$ GPa, and $G_{12} = 1.3$ GPa.

DISCUSSION

From the plots in Figs. 3 and 4 the average values of E_{11} are 22 and 33 GPa at 2.2 and 4.5 m/s, respectively. Though an increase in tensile modulus with strain rate has been observed before (10); the 50 percent increase found in this study seems too large to account for velocity effects alone. The effect of velocity may be attributed to the particular layup of the Scotchply. The 90 degree second ply should have a tensile strength somewhat lower than the resin itself; hence be of the order of 40 to 60 MPa. Very early in the impact event, this ply may fracture and delaminate from the specimen along with the first ply. This reduces the effective thickness by 15/17. Such delamination was, indeed, observed and was, particularly, frequent at large c/d . E_A is determined from the deflection which, in turn, is calculated from the energy absorbed by the specimen. Since the energy is arrived at by integration of the load-time curve, the influence of that delamination on the integral will depend on the time to fracture initiation, becoming more pronounced at longer t_i . When the low velocity data are corrected for a reduction in the effective thickness a better agreement is obtained with the 4.5 m/s results. Experiments to elucidate the influence of velocity in more detail are now in progress. Using the rule of mixture, the tensile modulus of the Scotchply composite was calculated to be 34 GPa ($E_{\text{glass}} = 76$ GPa; $E_{\text{epoxy}} = 6$ GPa; $V_f = 0.4$), which suggests that E_{11} in Eqs. 5 and 8 is the tensile modulus of the composite.

The shear modulus, G_{12} , was found to be between 1.1 and 1.3 GPa, which is about the reported shear modulus of epoxy resins, but not of composites. Using the torsion test method, Greszczuk (11) reported shear moduli of 1.3 GPa for an epoxy resin and 4 GPa for its glass fiber composite ($V_f = 0.5$). Shear moduli of composites reported in the literature are usually in the range of 2.5 to 10 GPa. Hence, it appears that G_{12} in Eqs. 5 and 8 approximates that of the resin. That was also the conclusion of Chambers and McGarry (8). Note that within the range of velocities of this study G_{12} appears to be independent of impact rate.

Fracture initiation energy density, w_i , is the minimum energy necessary to initiate a crack. It is a measure of the material ability to absorb energy and, hence, is of great interest for comparative evaluation of composite materials and design. In a previous study (12) the crack initiation energy was found to be independent of impact velocity. This also appears to be the case in this study: the difference between 2.2 and 4.5 m/s being statistically not significant. But the difference between w_i at $c/d < 7$ and $c/d > 9$ is statistically significant, probably reflecting the increased contribution of tensile effects (Eq. 8). Based on Charpy test data ($c/d = 4$) of unidirectional E-glass epoxy composite reported by Beaumont, *et al.* (4) we have calculated w_i to be 2.4 MJ/m³, an excellent agreement with

the result of this study. In Table 3 we have listed the fracture initiation energy density of several composite materials that have been tested previously (12). It should be noted that fracture initiation was predominantly in shear.

Quantitative correlations for the propagation energy, w_p , and material properties are, as yet, not available. w_p of the Scotchply composite does not appear to depend on velocity, but is strongly influenced by c/d as is evident from Tables 1 and 2. The large decrease is probably due to a transition from a shear dominated to a tension dominated failure. That shear failure results in high energy is well known. In a previous study (12), for example, the propagation energy of a unidirectional glass fiber-vinyl ester composite that failed in almost pure shear was found to be 39 MJ/m³ as compared to 13 MJ/m³ for a unidirectional graphite-vinyl ester that exhibited mostly tensile failure under the same testing conditions.

A puzzling failure was observed at spans of 10 and 15 cm. The fractured specimens can be classified into two groups, a sample of each is shown in Fig. 5. In the first group crack propagation was mostly in tension and w_p was low. For example, at 4.5 m/s and 15 cm span, w_p for that group (40 percent of specimens tested) ranged between 0.056 and 0.076 MJ/m³. In the second groups failure was mixed. A striking feature was the extensive delamination, or brooming, of the fractured specimens. Associated with these specimens were the load oscillations (see Fig. 2) and high values of w_p : 2 to 3.2 MJ/m³ at 4.5 m/s and 15 cm span. Why do specimens of the same composite fail in such markedly different ways? Pyrolysis ruled out the possibility of different glass content: 45 percent by volume was found in both groups. At present we think that it may be related to the construction of the Scotchply material. The second and sixteenth plies, being in 90° to the principal direction, probably cause a

Table 3. Composites Fracture Initiation Energy Density (Impact Velocity = 2.2 m/s; $l/d = 4-6.3$).

Material	w_i , MJ/m ³
XMC	1.0
Graphite-epoxy 0°/90°	1.1
Graphite-Vinylester, 0°	1.3
Glass-polyester, 0°	2.3
Glass-aminovinyl ester, 0°	2.5
Scotchply	2.5

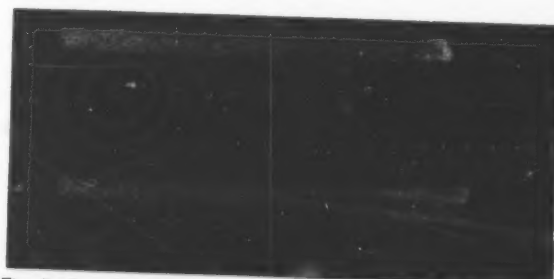


Fig. 5. Samples of specimens fractured at 15 cm span and 4.5 m/s showing: 1. Tensile failure, and 2. Tensile and shear failure.

domain of low shear strength. Evidence to that was seen in a number of specimens: rather than break in tension the outer two plies delaminated in unison with no apparent damage. The wide oscillations in the load are possibly indicative of irregular transient conditions in the impacted specimens that give rise to shear failure. Under what conditions exactly brooming and high w_p occur is not as yet clear.

CONCLUSIONS

The impact response of a unidirectional glass fiber composite and its ability to absorb energy in a three-point drop-weight impact are influenced by the composite's tensile and shear properties. Analysis of the impact response—a combination of tensile and shear deformation—has shown that the shear modulus, G_{12} , approximates the shear modulus of the neat resin; the tensile modulus is that of the composite, which is dominated by the fibers.

Both tensile stress and shear stress contribute to fracture initiation energy. Since both are influenced by the fibers, particularly the former, high volume fraction and high strength fibers are important for the fabrication of composites with high impact energy absorption. Finally, extensive delamination along the fibers is, usually, accompanied by high impact energy.

REFERENCES

1. S. G. Wogulis, B. W. Whitney, and D. R. Ireland, "Automated Data Acquisition and Analysis For Instrumented Impact Test," ASTM Symposium on Computer Automation of Materials Testing, Nov. 8, 1978, Philadelphia, PA.
2. D. R. Ireland, ASTM STP 563, 3-29 (1974).
3. J. M. Hodgkinson, N. S. Vlachos, J. H. Whitelaw, and J. G.

- Williams, *Proc. R. Soc. London*, A 379, 133 (1982).
4. P. W. R. Beaumont, P. G. Riewald, and C. Zweben, ASTM STP 568, 134-158 (1975).
5. L. J. Broutman and A. Rotem, ASTM STP 568, 114-133 (1975).
6. P. K. Mallick and L. J. Broutman, *J. Testing Evaluation*, 5, 190 (1977).
7. D. F. Adams and A. K. Miller, *J. Mater. Sci.*, 11, 1967 (1976).
8. R. E. Chambers and F. J. McGarry, ASTM Bulletin, No. 238, 38-41 (May, 1959).
9. T. H. Farebrother and J. A. Raymond, "The Stiffness Properties of Polymer Composites," in "Polymer Engineering Composites," Ed. M.O.W. Richardson, Applied Science Publishers, London (1977).
10. A. Rotem and J. M. Lifshitz, "Longitudinal Strength of Unidirectional Fibrous Composite Under High Rate of Loading," 26th Annual Conference RP/SPI, 10-C, February 9-12, 1971, Washington, D.C.
11. L. B. Greszczuk, ASTM STP 460, 140-149 (1969).
12. A. Golovoy, M. F. Cheung, and H. van Oene, "The Impact Behavior of Glass and Carbon Fiber Composites," 39th Annual Conference RP/SPI, 3-E, January, 16-19, 1984, Houston, TX.

NOMENCLATURE

- b = Specimen width.
 d = Specimen thickness.
 E_A = Apparent modulus.
 E_{11} = Tensile modulus.
 F_i = Load at fracture initiation.
 G_{12} = Shear modulus.
 l = Specimen length.
 t_i = Fracture initiation time.
 W_i = Fracture initiation energy.
 w_i = Initiation energy per deformed volume.
 w_p = Propagation energy per deformed volume.
 Δ_i = Deflection at fracture initiation.
 τ_{11} = Tensile stress.
 τ_{12} = Shear stress.

Conductive Composites Past, Present, and Future

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Conductivity of plastics and polymeric composites is reviewed. The use of various conductivity-enhancing fillers, such as graphite, metallized glass, or stainless steel fibers are discussed. Properties of composites containing rapid-solidified aluminum flakes are of particular interest.

INTRODUCTION

Plastics, once considered novel substitutes for traditional insulators such as glass and ceramics, are now being highly modified and used in applications demanding the performance of metal coupled with the processing economy of plastics. Complex, intricate shapes and parts consolidations are now possible, giving improved performance and cost effectiveness.

Plastics capable of conducting heat and electricity offer many advantages. They provide inherent EMI (electromagnetic interference) shielding to protect business machines, automotive and aerospace components, and computers from electromagnetic interference. They protect critical functions by giving continuous bleed of static charge. The conductive capability of modified plastics makes possible molded resistance heaters without the use of special heating elements. The property of thermal conductivity allows the molding of heat sinks as part of the cabinet and promotes the rapid dissipation of heat from products mounted in plastic enclosures. The volume (bulk) resistivity and thermal conductivity of various materials are compared in the graphs of Figs. 1 and 2.

HISTORY—INSULATORS TO CONDUCTORS

As Insulators

For most applications, thermal conductivity of plastics has been either disregarded or kept as low as possible. Applications in which the thermal insulating properties of plastics are used to advantage include power tools, athletic equipment, medical tools, and food service ware. This feeling of warmth to the hand due to the slow rate at which body heat is conducted away is physiologically pleasing and is frequently the major reason for the use of a plastic, i.e. tool handles and the like.

Plastics are also well known for use as electrical insulators. Applications which began many years ago using thin mica sheets have been replaced by thin films of polyester, polycarbonate, and many other electrical grade resins.

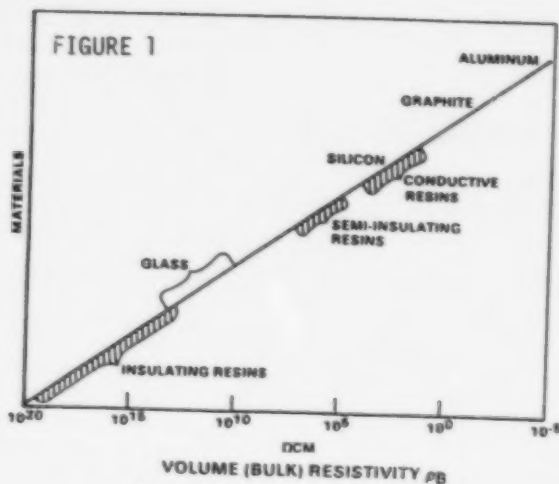
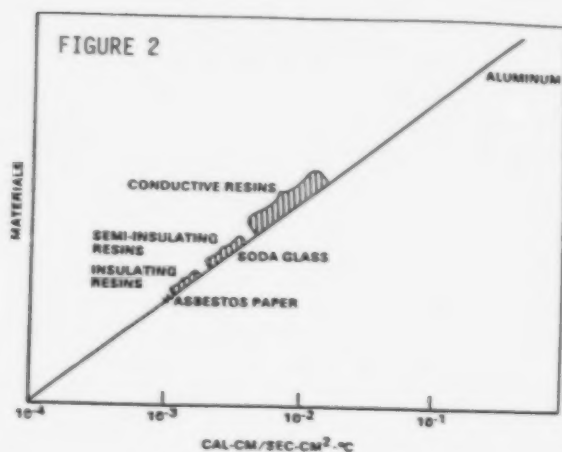
Applications for electrical resistivity can take us back to the same power tools discussed earlier. The switch from die cast drill and saw housings started the "double insulated" concept, and even allows the use of bosses as tie points for the joining of hot electrical wires. Plugs, electrical connectors, and wire and cable insulation all require a high degree of resistivity.

As Semi-Insulators

Most plastics can be changed into partially conductive materials, "semi-insulators" with the addition of certain modifiers or by special treatments. Glass, while usually added as a reinforcing agent to improve tensile strength and modulus properties of a composite, also increases the thermal conductivity. The normal range of conductivity for base polymers is 4 to 8×10^{-4} cal-cm/sec-cm²-degrees C; 20 to 30 percent glass-reinforced versions increase to 6 to 10×10^{-4} . Talc-filled versions may show virtually no change in thermal conductivity. Metal powders, iron and aluminum, can effectively increase heat transfer through a resin, and such materials are used at high loadings, often over 50 percent by weight. Applications include grinding wheel compounds and heat sinks.

Semi-insulators in the electrical area include those plastics filled with structured conductive carbon black or graphite powder, and newly developed polymers doped with modifying agents which can be incorporated directly into the polymer chain backbone itself. This class of products will usually exhibit bulk resistivity in the range of 10^4 to 10^6 ohm-cm at reasonable loading levels. By comparison, silicon, a semi-conductor, has bulk resistivity of 8×10^2 ohm-cm (1).

In this range of conductivity, applications as static dissipators become viable. While base polymers could develop a large static charge through sliding contact between moving parts, the semi-insulating grades can dissipate the charge through a slow leaking process. Gears, spindles, guides, and parts of sensitive electrical equipment currently use these modified grades.

Fig. 1. Volume (bulk) resistivity ρ_b .Fig. 2. Thermal conductivity λ .

As Conductors

The step beyond the powdered fillers and modified resins is those resins whose property profiles are changed dramatically by the incorporation of high aspect ratio conductive modifiers. This family includes metallized glass fibers, graphite fibers, rapid solidified aluminum fibers and flakes, and drawn stainless steel fibers.

In order to be used effectively, these modifiers must be amenable to the process intended. The initial high aspect ratio of a long brittle material is quickly reduced in the tortuous high shear environment of extrusion and injection molding, while the particles, short to begin with, give up the efficiency of greater aspect ratio. In all cases, efficiency of these modifiers is dependent on the aspect ratio of the particle in the final molded part.

Graphite fibers, both pitch and polyacrylonitrile (PAN), have been incorporated into thermoplastic molding compounds for physical property enhancement, but since the compounding process results in fiber breakup, dramatic improvements are seen only in highly loaded formulations. Resins with 30 percent graphite fibers exhibit high modulus and

enough electrical conductivity for some EMI shielding applications. The major limitation is in cost effectiveness.

Glass fibers metallized by vacuum deposition or dip coating with aluminum or nickel have been tested for electrical and thermal property enhancement. These products like the carbon fibers need to be processed as little as possible to avoid particle break-up in use. When employed in SMC and some BMC compounds, sufficient aspect ratio remains to give much better thermal conductivity than glass alone, coupled with electrical conductivity.

Wire drawn stainless steel fibers were developed for use in fabrics to dissipate static charges that build up in carpets and clothing. A unique process allows the drawing down of stainless steel to very fine diameters (4 microns) that have high initial aspect ratios.

As with any high aspect ratio modifier, electrical conductivity can be achieved with a low loading percent (7 to 10 percent by weight). The same rule of maintaining the aspect ratio of the modifier during compounding and molding applies, and the high cost of the chopped stainless steel fibers coupled with relatively low shielding values of the composites (20 to 30 dB) have limited their usage.

The fourth type of high aspect ratio conductive modifier is based on the development by Battelle Memorial Institute to make amorphous metal wire, ribbon, and particulates through the quick quench (10^6 °C/deg/sec) process. While not all metal alloys processed in this way are truly amorphous, even the crystalline forms are micro- or cryptocrystalline in form, retaining some of the advantages of fatigue and corrosion resistance, and ductility. Although many alloys based in iron, nickel, copper, tin, gold, silver, and platinum have been made, the material proven to be most economical and adaptable for use as a filler/modifier for thermoplastic and thermoset resins is rapid-solidified aluminum flake. It has the advantages of fatigue and corrosion resistance as well as ductility, low abrasion, and moderate cost.

Depending on volume loading and compounding technique, the volume resistivity of polymers exhibiting 10^{15} to 10^{18} ohm-cm can be reduced to 10^3 to 10^{-3} with the addition of the Transmet rapid solidified flakes (1).

CONDUCTIVE COMPOSITES TODAY

General

Since conductive composites are relatively new in volume applications, and some of the composites mold with a resin rich surface, it is appropriate to discuss some definitions and testing techniques.

Most people are familiar with resistance testing of materials that have an electrically conductive surface such as metals, conductive paints, and others. The measurement is surface resistivity and is expressed as ohms per square.

Conductive composites, along with metals whose ability to conduct electricity and hence shield against EMI/RFI (electro-magnetic interference/

radio frequency interference), are measured by volume (bulk) resistivity and expressed as ohm-cm. Volume resistivity is denoted as ρ_B .

Testing

Contact Area

By their nature, composites are mixtures or laminations of conducting particles or layers of a conducting material suspended between or mixed into an insulating matrix.

In Fig. 3 A, pointed probes could miss contact with the particulate filler, hitting a highly insulating zone and giving the impression that the composite as a whole is highly insulating. Large contact areas (4 cm² and larger) can overcome this deficiency in most homogeneous composites. However, in those which develop a resin-rich skin, which effectively insulates all particles from direct contact with the test probe, the conductivity through the test part is due to capacitive coupling to the internal conductive network, thus conductivity increases at higher frequencies.

In Fig. 3 B, the conductive component layered on one side of, or between two layers of, the insulating matrix, may read a volume resistivity (ρ_B) equal to the highly insulating matrix even with large contact probes. Surface resistivity (ρ_s) measured in ohm/square will give meaningful results only in the case of an exposed conductive surface. In this test, probes 1 unit square are positioned 1 unit apart. The resistance in ohms is reported in ohms per square, and relates to ρ_s by the formula below where t is thickness (2).

$$\rho_B = \rho_s t^{-1}$$

Anisotropic Resistance

As in Fig. 3 A, a homogeneously dispersed conductive additive, when molded into a composite part cubic in form, would exhibit equal resistivity in three orthogonal directions. This is not normally the case, as in a typical molding some flow occurs which orients systems whose filler component has an aspect ratio greater than 1. Typically orientation is parallel to the plane of the part, giving higher conductivity in this direction, often by a factor of 10, greater than in the direction normal to the plane. For uses which demand conductivity in the

plane of the part (electromagnetic interference shielding, resistive heating, etc.), resistance must not be measured through the thickness (normal to the plane), but in the plane. This can be accomplished in several ways, two of which are discussed in the following paragraphs.

Volume (Bulk) Resistivity Test Methods

Volume resistivity of a composite specimen can be measured in several ways. In the common method, contact is made through the resin-rich top layer into the filler-rich area beneath.

The method of Fig. 4 A involves a contact equipped with sharp pyramids screwed into the plaque 0.3 to 1.0 mm. The voltage drop at 500 mA is measured and resistance is calculated as (3):

$$\rho_B = R = E/I$$

The resistivity, ρ_B , is then calculated by (3):

$$\rho_B = R \cdot A/L$$

Although this does not take into account current density variations (fringing) as does the method of Fig. 4 B, the equation is valid for the degree of accuracy possible.

The method of Fig. 4 B requires a sample machined into a washer shape (OD = 100 mm, ID = 45 mm). The edges are then coated with a conductive paint, allowed to dry, and inserted into a flexible walled holder which contacts inner and outer diameters. The measured resistance is then inserted into the formula (3):

$$\rho_B = (R_{utcm}) 7.64$$

From either test method, the resistivity can be used to estimate the average Shielding Effectiveness (SE) between 0.1 and 1000 MHz, by using the graph in Fig. 5 (3).

In cases where the filler is platelet or spherical, isotropic conductivity in the plane allows either test method to be used. However, if low concentrations of high aspect ratio fibers are used, their orientation in the direction of flow can result in conductivity in only one direction. Thus, with these materials, conductivity is possible without good EMI shielding, and the relationship of ρ_B to SE would be changed greatly due to the low efficiency of the fibers with respect to shielding.

The Resin Choice

Homogeneous conductive composites are plastic resin formulations based on a standard insulating polymer ranging from the polyolefins and simple styrenics on up through the more sophisticated engineering resins, and encompass both thermoplastic and thermoset types. These, when combined with electrically conductive additives, exhibit properties somewhere between the two end points of a pure polymer and a pure additive.

The choice of a base resin for the conductive composite will depend upon the engineer's need for physical, heat, and chemical properties. In typical business machine housings and portable elec-

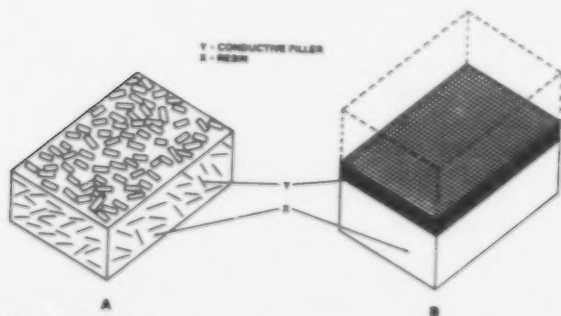


Fig. 3. Distribution of conductive elements in a homogeneous and a laminar structure.

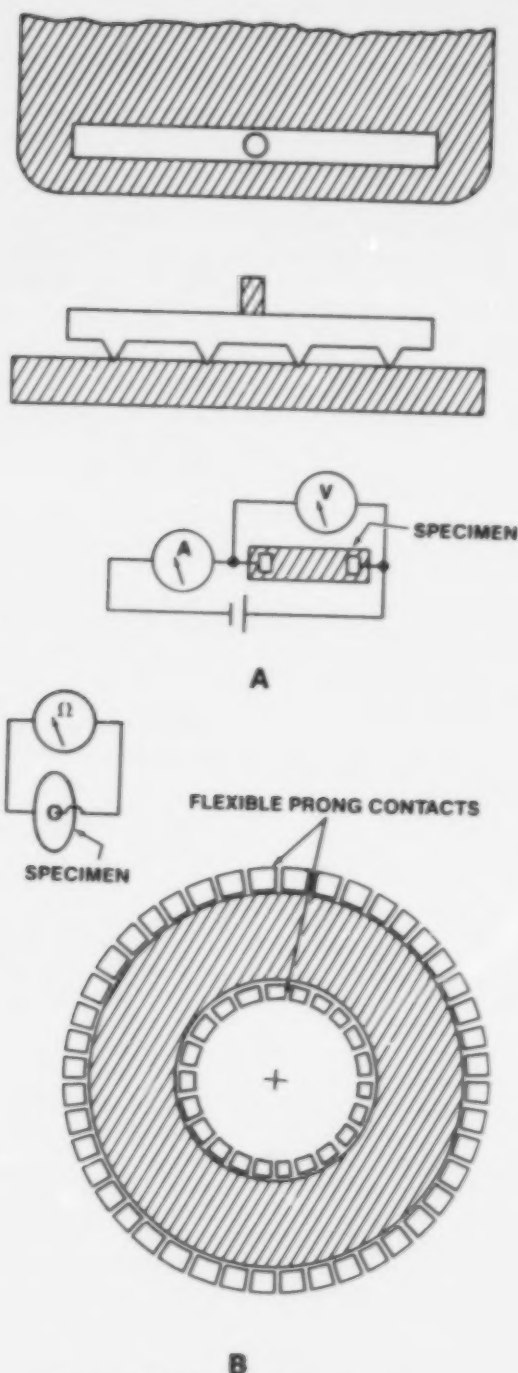


Fig. 4. Testing for electrical conductivity.

tronics, the requirements are frequently for rigidity and impact strength, while those housings for microprocessors which will find their way into the adverse environments of chemical processing plants might find chemical resistance to be of paramount importance. Or the most aggressive of atmospheres, that encountered by under-the-hood electronics in the automotive area, will demand reasonable physical properties, high heat distortion, and good chemical resistance.

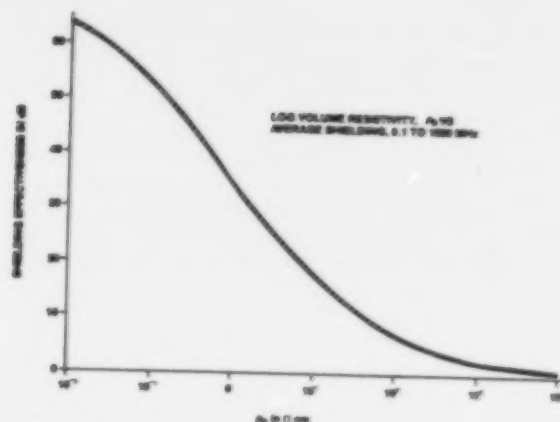


Fig. 5. Volume resistance relation to shielding effectiveness.

The second consideration in a resin choice is economics. In many cases, two resin systems may be sufficiently close in property profile but either can be used, especially taking into account the enhancing feature of the fillers to be considered. Thus, a 40 percent flake modified polypropylene would have a higher heat distortion than an unmodified PBT or nylon.

In general when high heat and/or chemical resistance is required, a crystalline resin is used for the base, while amorphous resins are more popular in applications that require low mold shrinkage and good dimensional stability. With all of the alloys and blends available today, the choice of a base resin for a conductive composite is almost unlimited.

The Filler Choice

Previous discussions on conductive modifiers have shown that structured carbon black powders added to resins will lower the volume resistivity of the composite to 10^3 to 10^8 ohm-cm and are suitable for many static dissipation or antistatic applications. The primary drawback is the reduction of physical properties at loading levels above 10 to 15 percent, and the black color which may rub or slough off during handling of parts.

Precious metal powders have also been used, but these have had limited markets because of their high cost. The largest use has been of electrically conductive elastomers for EMI shielding gaskets and a few applications for conductive epoxy adhesives.

Graphite fibers and the newer nickel plated graphite fibers will, when properly formulated, produce a conductive composite with conductivity in the range of 10^{-1} to 10^1 ohm-cm. These fibers not only provide conductivity to the composite, but also furnish considerable reinforcement as well. When added to engineering resins, graphite fibers give a product with a property profile suitable for aerospace applications in which both its inherent EMI shielding capability and high modulus warrant their high cost. The nickel coated graphite fibers will impart the same electrical properties to a com-

posite as the uncoated fibers at about fifty percent of the loading (15 to 20 percent versus 30 to 40 percent), but the additional cost of the nickel coated fiber still inhibits its usage in high volume commercial applications.

Stainless steel fibers achieved a high level of interest as a conductive modifier when it was thought that, due to the low fill level, "as molded" colored parts could be produced in existing tooling. Unfortunately only the heavily textured surfaces in dark colors did not show the adverse effects of the steel filler, and since there were no improvements in physical properties, such as higher modulus or heat distortion temperatures, the high cost and low shielding values have dampened the interest level.

Rapid-Solidified Aluminum Flakes by the quick quenching process have been used since 1979 combined with a variety of resin matrices.

The Transmet process of Rapid Solidification produces aluminum flakes that are consistent in shape and size (1 mm by 1.2 mm by 30 microns). They are platelet, ductile in nature, and highly resistant to corrosion. Being platelet in form, the flakes tend to orient with the flow. This can allow the formation of a conductive network of flakes at a lower loading. Flakes do not agglomerate at corners and bosses as fibers may, and they exhibit planar isotropic qualities that reduce part warping. Ductility makes the flakes more adaptable to the compounding and molding processes. It allows them to flow with the composite through intricate molds without breakage or loss of conductive properties.

Typical formulations for electrically conductive composites based on the rapid solidified flake contain the modifier in the range of 18 to 22 volume percent. Since electrical conductivity is determined by volume loading and not weight percent, this conversion must be made for each specific gravity resin. As an example, a low density polymer such as a polypropylene would need 46 weight percent to equal the 22 volume percent for high conductivity. On the other hand, a higher density product such as a PVC would require only 37 weight percent for the same 22 volume percent loading.

In addition to the volume loading, the high aspect ratio of the flake additive must be preserved. This flake integrity can be adversely affected by high shear and overwork in the compounding process. An extremely high aspect ratio product tends to bend or break in processing and its efficiency is reduced. On the other hand, a product that is overworked and reduced in aspect ratio is highly inefficient and, as it approaches the limit of a chunky or spherical particle, is unable to render a conductive composite even at extremely high loadings of 80 percent or more. Although compounding must be gentle enough to insure minimal degradation of the flake, it must be sufficient to achieve a uniform dispersion within the melt. This can be achieved on compounding equipment used by compounders today.

Electrical conductivity in an aluminum flake modified composite depends on the formation of an internal network at some critical concentration. At

this conductivity breakover point, the overall resistivity is dramatically reduced, as shown in Table 1.

Below breakover the polymer has improved thermal conductivity, but since there is an array of conductive but noncontacting particles the polymer exhibits high electrical resistivity. When continuity is checked in series with a light bulb, the light will be either off or at full brightness, depending on whether the concentration is below or above the breakover point. A composite modified with carbon black or graphite fiber in the same test would cause the bulb to glow with varying brightness, indicating a low level of conductivity. Figure 6 illustrates how aluminum flake gives the highest conductivity at the lowest volume loading.

Economies

Whereas a choice of resin system for a conductive composite is based on the environmental usage of a conductive part, the choice of a conductive modifier will more often be based on its cost effectiveness. Since the majority of volume applications today are involved with EMI/RFI shielding of electronic enclosures, and most people are aware of the price pressures involved in that market, Table 2 should assist in the choice of a conductive modifier/filler.

While each of the conductive modifiers imparts separate properties to a conductive composite, none of them other than the Rapid-Solidified Alu-

Table 1. Resistivity of Aluminum Flakes.

Weight % of Al Flakes	Resistivity (ohm-cm)
5%	10^{15}
10%	10^{13}
15%	10^8
20%	10^2
25%	10^0
30%	10^{-1}
35%	10^{-2}
45%	10^{-3}

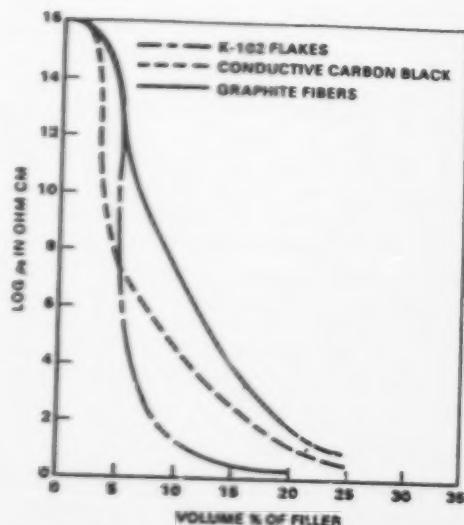


Fig. 6. Volume resistance relation to filler volume.

Table 2. Cost of a Conductive ABS Composite with Various Modifiers.

Modifier	Cost (\$/lb)	Wt % Used	\$/lb of Composite	\$/cu in	Average SE	dB/\$/cu in
Graphite Fiber (PAN)	25.00	40	15.00	0.659	45 dB	68
Graphite Fiber Nickel Coated	50.00	15	9.00	0.400	40 dB	100
Stainless Steel	50.00	8	4.75	0.210	35 dB	166
Aluminum Flake	2.55	40	2.75	0.152	50 dB	329

minum Flake have the important combination of cost effectiveness and EMI/RFI shielding along with extremely high thermal conductivity. Thermal conductivity is the major benefit of conductive composites of the future.

TOMORROW'S CONDUCTIVE COMPOSITES

General

The modifiers in use today will continue to dominate the scene, with each seeking its level of cost effective benefit. Inherently conductive polymers are a number of years away, and the costs are still questionable.

Applications utilizing BMC and SMC (bulk and sheet molding compound) technology will use plated glass and graphite fibers, particularly in woven mat form, as their conductive backbone. Injection molded thermoset and thermoplastic conductive composites will use most of the earlier mentioned conductive modifiers, either alone or in conjunction with others.

Structured carbon black and antistatic additives may see stainless steel fibers, used in low levels of concentration, join them in ESD applications. The graphite fibers will dominate in military and aerospace applications where the need for ultra high physicals in addition to good electricals will justify their cost. Aluminum flake/fiber modified composites have the proper profile of physical properties, economics, and shielding effectiveness to become the primary modifier for electronic enclosure applications.

A number of commercial applications have proven the ability of flake filled composites to compete with the alternative methods of shielding that were offered in the past. Secondary methods of shielding will continue to be used in the future, but will have to contend with the newer design and fabrication technology of aluminum flake filled composites such as co-injection molded parts that have a Class A surface inside and out, along with the dual molding or overlay molding process.

In any event the rush to solve the EMI/RFI problem may be somewhat short-lived. A number of electronics manufacturers have stated that within 8 to 10 years it will be economically feasible to eliminate the EMI/RFI problems at the source and thereby eliminate the need for shielding whether through conductive composites or secondary operations.

Where To From Here?

As a higher degree of reliability and understanding of conductive composites comes about, there will be more direct substitution of conductive com-

posites for metals without going through the stage of using an unfilled plastic and then applying secondary operations to make the unfilled parts acceptable. Of major importance in allowing this transition to take place will be composites with an extremely high thermal conductivity.

Rapid solidified flake modified plastics can be used to advantage in many applications where heat dissipation is necessary. Heat sinks need not be a special piece of hardware. Now they can be molded as part of the equipment housing at virtually no extra cost.

Grinding wheels and moving parts, which generate heat at a localized portion, can absorb the heat energy and dissipate it across the entire part when they are made from flake modified plastics. Table 3 compares aluminum flake with aluminum powder filled phenolic in both thermal and electrical conductivity.

Tooling for blowmolding, vacuum forming, sheet molding, and mat molding made of epoxy filled with aluminum flake has a higher thermal conductivity, a smoother surface, and longer life than aluminum powder filled epoxy. The rate of heat conduction through a flake modified composite can be controlled between the extremes of unfilled resin and pure aluminum. (Fig. 7).

The same anisotropic phenomena that gives aluminum flake composites higher electrical conductivity in the plane of flow applies to increased thermal conductivity as well. Standard ASTM-C177 testing, which is generally done perpendicular to the plane of flow, will show an eight to ten fold increase (from $4-6 \times 10^{-4}$ cal/sec-cm²-degrees C to $35-45 \times 10^{-4}$ cal-cm/sec-cm²-degrees C). Testing of flake modified plaques in the plane of flow have shown derived thermal conductivity values of 240×10^{-4} cal-cm/sec-cm²-degrees C or 48 times higher than the base resin (4).

The report on the thermal conductivity relationship of aluminum flake modified conductive composites versus other materials, including the mechanism which allows this improvement, will be published by Transmet at a later date. Some of the early testing involved the material's ability to dissipate heat from a 9.7 BTU/hr. heat source. Selected results are in Table 4 (5).

Table 3. Comparison of Aluminum Flake Versus Aluminum Powder.

	Specific Gravity	Electrical Resistivity (ohm-cm)	Thermal Conductivity (cal/sec/cm ² /C)
Powder	1.85	$>10^6$	10×10^{-4}
Flakes	1.85	10^{-1}	40×10^{-4}

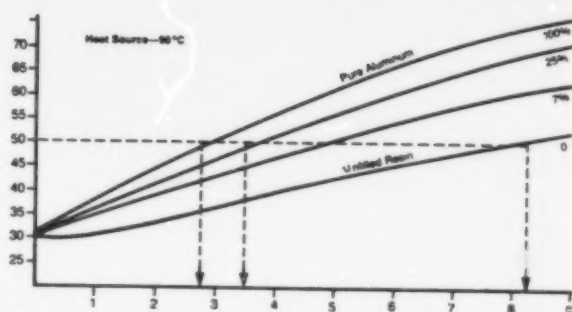


Fig. 7. Time-temperature rise, selected flake loadings (volume percent).

Table 4. Percent of Q (9.7 btu/hr) Dissipated by Conduction.

	T	% Q_{con}	Q_{con} Normalized To Al
Aluminum	20	83.8%	100%
Flake Filled Composite	30	73.2%	87%
ABS	71	21.3%	25%
Urethane Foam	86	0%	0%

The Market

While EMI/RFI shielding may lose some of its impetus in satisfying governmental regulation with the advent of quieter electronics, many manufacturers must still protect their sensitive electronic components from outside noise. Therefore enclosures will continue to be produced that require shielding of some manner, and conductive composites can be the major thrust of a new design concept in an expanding market. Different studies have predicted the requirements for conductive composites to be between 50 and 60 million pounds annually by 1987.

As electronics get more complex they tend to create more heat, and the ability of a material to dissipate this heat while providing inherent shielding assures aluminum flake a major portion of the rapidly expanding conductive composite market. In fact, a number of applications that require only thermal conductivity are already in existence with flake filled products.

No discussion of markets for thermally conductive composites would be complete without including automotive. Cars are getting smaller and lighter. This requires a conversion from heavier metals to plastics. In addition, the smaller engines run hotter

in smaller confines. Until recently one of the detriments in converting metals to plastic has been the lack of ability of plastics to conduct heat, but the same composites that satisfied the heat problems in the electronic industry are now solving problems in the automotive industry.

Other markets that shouldn't be overlooked are varied. Conductive composites as electrical conductors have been used in applications requiring resistive heating. The narrow band of resistivity needed to control a reliable resistive heater is difficult to control during compounding and molding, therefore most work in this area is with SMC or hand layup polyesters. Aluminum flake filled conductive composites have been used as thermal conductors in the food industry for candy molds and egg poachers.

CONCLUSION

The next decade will see uses for conductive plastic composites that should expand the volume required well beyond current forecasting capabilities. There will be additional resins and alloys used to satisfy certain environmental or structural needs of new conductive composites. The conductive modifiers or fillers will probably be the same or various combinations of the ones currently in use.

Designers should have a broad variety of resin/modifier combinations to choose from. As applications incorporate conductive composites into their original design, the composites with the best cost/performance properties will continue to grow regardless of the onslaught of inherently conductive polymers and the reduced need for EMI/RFI shielding.

NOMENCLATURE

EMI/RFI	= Electromagnetic interference/radio frequency interference.
ρ_B	= Volume (bulk) resistivity.
ρ_S	= Surface resistivity.
SE	= Shielding effectiveness.
BMC	= Bulk molding compound.
SMC	= Sheet molding compound.

REFERENCES

1. R. M. Simon, *Symposium on Electrically and Thermally Conductive Plastics*, London 1982.
2. D. L. Stutz, Battelle Memorial Institute, *Comparison of EMI Shielding Methods*, 1981.
3. *Technical Transmission TM101-3*, Transmet Corp., 1983.
4. *Testing at Battelle Pacific Northwest Laboratories*, 1984.
5. *Technical Transmission TM402*, Transmet Corp., 1984.

SI METRIC UNITS

The following list shows the names, symbols, and equivalence of the more common quantities allowed in the SI metric system. The prefixes and symbols for the more common multiple units are also shown. Neither list is complete. Full details are given by F. S. Conant, *Polym. Eng. Sci.*, 17, 222 (1977). A table of the more frequently needed conversion factors required to use the SI system is also shown. This journal prefers that SI metric units be employed in manuscripts submitted for publication.

Units and Symbols

Quantity	Name	Symbol	Equivalent to:
Length	metre	m	—
Time	second	s	—
	minute	min	—
	hour	h	—
	kilogram	kg	—
Mass	ampere	A	—
Electric current	radian	rad	—
Plane angle	litre	L	10^{-3}m^3
Capacity	hertz	Hz	s^{-1}
Frequency	newton	N	$\text{m} \cdot \text{kg} \cdot \text{s}^{-2}$
Force	pascal	Pa	$\text{N} \cdot \text{m}^{-2}$
Pressure, Stress	joule	J	$\text{N} \cdot \text{m}$
Energy, Work, Heat	watt	W	$\text{J} \cdot \text{s}^{-1}$
Power	pascal second	Pa · s	$\text{N} \cdot \text{s} \cdot \text{m}^{-2}$
Viscosity, dynamic			

(The following units should *not* be used: micron, angstrom, dyne, erg, calorie, poise, or stoke.)

Multiple Units

Prefix	Symbol	Equivalent to:
giga	G	10^9
mega	M	10^6
kilo	k	10^3
deci	d	10^{-1}
centi	c	10^{-2}
milli	m	10^{-3}
micro	μ	10^{-6}
nano	n	10^{-9}

Conversion Factors

Force: $1 \text{N} = 10^5 \text{ dynes} = 1.02 \times 10^{-1} \text{ kgf} = 2.248 \times 10^{-1} \text{ lbf}$.

Pressure, Stress: $1 \text{ Pa} = 10 \text{ dyne cm}^{-2} = 7.5 \times 10^{-3} \text{ mm Hg} = 10^{-5} \text{ bar} = 1.02 \times 10^{-5} \text{ kg cm}^{-2} = 1.45 \times 10^{-4} \text{ psi}$.

Energy: $1 \text{ J} = 2.387 \times 10^{-1} \text{ cal}$.

Viscosity: $1 \text{ Pa} \cdot \text{s} = 10 \text{ poise}$.

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Mo.	Yr.	Mo.	Yr.				
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(S)	Date	

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According to Young, et al. (1)...

- In the list of references the general style is as follows:

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1. S. S. Young, J. L. White, E. S. Clark and Y. Oyanagi, *Polym. Eng. Sci.*, 20, 798 (1980).

The journal name and volume are to be underlined and the year is placed in brackets. The issue number is given only when needed for identification. The article name is eliminated unless the reference is unclear without it.

For books: The title to be spelled out in full.

5. H.-G. Elias, "Macromolecules," Ch. 1, Vol. 2, Plenum Press, New York (1977). (Include the state when the city is not identifiable.)

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Continued from Front Cover

- 494 T. KANAMOTO and A.E. ZACHARIDES/Morphological Studies of Oriented Ultra-High Molecular Weight Polyethylene with Enhanced Planar Mechanical Properties
- 497 E. EISE, J. CURRY, and J. FARRELL/Processing of Reinforced Plastics using Multi-Screw Compounders
- 502 A. GOLOVOY and H. VAN OENE/Impact Energy Absorption of Unidirectional Glass Fiber-Epoxy Composites
- 507 R.A. CROSSMAN/Conductive Composites Past, Present, and Future



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